Free fat and physical structure
of spray-dried whole milk

Proefschrift
ter verkrijging van de graad van
doctor in de landbouwwetenschappen,
op gezag van de Rector Magnificus, mr. J. M. Polak,
hoogleraar in de rechts- en staatswetenschappen
van de westerse gebieden,
te verdedigen tegen de bedenkingen van een commissie
uit de Senaat van de Landbouwhogeschool te Wageningen
op vrijdag 15 oktober 1971 te 16 uur

door

T. J. Buma

Stellingen

1. De methode voor de bepaling van de ruimtelijke verdeling van de voornaamste componenten in melkpoederdeeltjes, welke werd toegepast door zowel Bockian en medewerkers als Holsinger en medewerkers, is onjuist.

> A. H. Bockian, G. F. Stewart en A. L. Tappel, *Food Res.* 22 (1957) 69
> V. H. Holsinger, K. K. Fox, M. K. Harper en M. J. Pallansch. *J. Dairy Sci.* 47 (1964) 964.

2. De conclusie van E. L. Jack, dat de lactose in verstuivingstaptemelkpoeders geen bijdrage levert tot de volumecontractie, die plaats vindt bij het oplossen van zulke poeders, is niet gerechtvaardigd.

> E. L. Jack, *J. Dairy Sci.* 22 (1939) 353 en 761.

3. Tegen de door Samhammer voorgestelde methode voor de beoordeling van de oploseigenschappen van melkpoeders kan een belangrijk bezwaar worden aangevoerd, waardoor deze methode niet zonder meer kan worden toegepast op vollemelkpoeders.

> E. Samhammer, *Milchwissenschaft* 21 (1966) 413.

4. Bij de polarimetrische bepaling van de zuiverheid van α-lactose. 1 aq. en β-lactose dient men zich er rekenschap van te geven dat de in de meeste handboeken opgegeven waarden voor de specifieke rotaties van deze stoffen, minder nauwkeurig zijn dan de getallen suggereren.

> R. Jenness en S. Patton, Principles of dairy chemistry, John Wiley & Sons, New York, 1959, p. 75.
> B. H. Webb en A. H. Johnson, Fundamentals of dairy chemistry, AVI Publ. Comp., Westport, 1965, p. 228.

5. Bij het droog mengen van micro-ingredienten in voormengsels voor vee-voeders dient rekening te worden gehouden met de mogelijkheid dat hierbij interacties kunnen optreden die de voedingswaarde van het voeder aanzienlijk kunnen verlagen.

6. Door Appleman werden krommen gepubliceerd die het verband aangeven tussen de relatieve vochtigheid van de atmosferische lucht en het grondzicht, met het doel om op grond van de te verwachten luchtvochtigheid het grond-zicht te kunnen voorspellen. De praktische waarde van de krommen moet echter worden betwijfeld.

H. Appleman, *Bull. Am. Met. Soc.* 39 (1958) 31.

7. Het schoonmaken van procesapparatuur in de voedingsmiddelenindustrie dient tegenwoordig te worden beschouwd als een volwaardig, geïntegreerd bestanddeel van het totale produktieproces en verdient daarom zowel in de apparatenbouw als bij het technologisch onderzoek een centrale plaats.

8. Aan het vak 'Proeven en toestellen' in het examenprogramma van de akte Wis- en Natuurkunde voor leraren bij het beroepsonderwijs dient grotere waarde te worden toegekend, daar dit vak in belangrijke mate kan bijdragen tot de vorming van de aanstaande Natuurkunde-leraren.

9. In het studieprogramma voor de Nijverheidsakte Wis- en Natuurkunde zijn voor het onderdeel 'toestellen' enkele instrumenten opgenomen waarvan de werking niet voldoende bekend is. Zij dienen te worden vervangen door andere.

10. Een centrale basisopleiding voor vertegenwoordigers in de handel in weten-schappelijke instrumenten zou het overwegen waard zijn.

11. De vakantievreugde van vele Nederlanders zou verhoogd kunnen worden door ieder jaar vroegtijdig deskundige en aangepaste voorlichting te geven over de meteorologische wetmatigheden die het lokale klimaat in de belangrijkste vakantiegebieden van Europa bepalen.

Proefschrift van T. J. BUMA,
Wageningen, 15 oktober 1971.

Aan mijn vader
Aan mijn vrouw en kinderen

Voorwoord

Het experimentele werk dat ten grondslag ligt aan dit proefschrift, werd nage-
noeg gelijktijdig begonnen met mijn toetreding als wetenschappelijk medewerker
tot het Research Laboratorium van de Coöperatieve Condensfabriek 'Friesland'
in September 1959. Het onderzoek betrof de fysische eigenschappen van ver-
stuivingsvollemelkpoeders en de relaties ervan met andere poedereigenschappen.
In de loop van de tijd werden enkele resultaten die daarvoor geschikt waren,
gepubliceerd. Met het oog op dit proefschrift werd tevens kort geleden een
serie van acht artikelen geschreven met als centraal thema 'Vrij vet in ver-
stuivingsvollemelkpoeders'. Een deel van het beschreven werk werd reeds lang
geleden uitgevoerd.

Dit proefschrift bestaat uit bovengenoemde serie, aangevuld met twee
andere publicaties die er min of meer een geheel mee vormen. Vijf andere ar-
tikelen* die ook betrekking hebben op verstuivingsvollemelkpoeders, werden
niet opgenomen in het proefschrift omdat die slechts zijdelings te maken hebben
met het 'vrij vet', ofschoon van de resultaten wel gebruik is gemaakt.
De directie van de CCF ben ik dankbaar dat zij tot nu toe steeds de gedragslijn
heeft gevolgd toestemming te verlenen voor de publicatie van bepaalde resul-
taten van wetenschappelijk onderzoek.

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* T. J. Buma, The true density of spray milk powders and of certain constituents. *Neth. Milk
  Dairy J.* 19 (1965) 249–265.
T. J. Buma, The physical structure of spray milk powders and the changes which take place
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  Neth. Milk Dairy J. 23 (1969) 124–127.
T. J. Buma, Determination of crystalline lactose in spray-dried milk products. *Neth. Milk
  Dairy J.* 24 (1970) 129–132.

Contents

1. General introduction and brief review of literature

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Abstract

Many workers have observed that only part of the fat in spray-dried milk can be extracted by fat solvents under standardized conditions. This fat is usually called 'free fat' and has been related to other powder properties which are of practical importance.

Contradictory results obtained by different workers have raised doubts concerning the practical significance of free-fat content. Moreover the explanation generally accepted in the literature, that free fat is 'unprotected fat' mainly situated on the particle surface, is not altogether satisfactory.

An experimental study of the properties of free fat and its relation to powder properties of practical significance was carried out. The results of this study are described in a series of articles in this journal. In this first report a general outline of the problem and a brief review of the literature is given.

1.1 General introduction

Since Holm et al. (1) in 1925 related the quality deterioration of whole milk powders during storage to the free-fat content the latter quantity has been determined by many workers concerned with production or quality control of dried whole milk. In the meantime also other authors have correlated the free-fat content of dried milk with powder properties of practical importance. These are:

a. The keeping quality, particularly the development of tallowiness or oxidation flavour of the milk fat during storage (1,2,3);

b. The dispersibility or the wettability of whole milk powders during reconstitution (4–9);

c. The cream rising of milk fat during and after dried milk has been reconstituted (2, 10–12);

d. The stickiness of whole milk powders (13, 14).

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In all these cases a high free-fat content was considered to be unfavourable.

Usually free fat is defined as that fraction of the fat which can be extracted with organic solvents under standardized conditions. Unfortunately very different conditions have been used by various workers and as no systematic evalution of methods was carried out, their results may not be comparable.

The term 'free-fat' originates from Holm et al. (1) who considered it as 'fat not protected by a protein film'. Sometimes the term 'liberated fat' or 'unprotected fat' is used. In our opinion no strict evidence is available that the free fat of spray-dried whole milk consist of such unprotected fat.

Several authors (7, 9, 15, 16) suggested that the unprotected fat globules are able to coalesce and to form patches or a layer of unprotected fat on the surface of the powder particles. If the free fat in spray-dried milk is considered as mainly consisting of surface fat, it is reasonable to assume that it influences the wettability, dispersibility and stickiness of the powder, because these are specific surface properties.

However results obtained by some workers indicate that there is no correlation between free fat and the above powder properties. Moreover other phenomena, such as the influence on the free-fat content of homogenization of the concentrated milk prior to spray drying, cannot be explained satisfactorily by considering the free fat to be located on the particle surface.

At an earlier date we concluded from our experiments (17) that at least part of the free fat is actually located inside the powder particles and we therefore related the occurrence of free fat in spray-dried whole milk to the presence of micropores in the powder particles (18).

In view of the above discrepancies it was thought useful to carry out a systematic experimental study of the properties of free fat and its relation with powder properties of practical importance. The results will be published in a series of articles in this journal.

In the following we review the literature on free fat in relation to the physical characteristics of spray milk powder particles and to the processing conditions which affect the free-fat content. The other subjects are reviewed in the subsequent papers.

1.2 Free fat and the physical structure of spray-dried whole milk particles

Since the discovery that only part of the fat in spray-dried whole milk can be extracted by fat solvents (1), many workers have tried to provide an explanation of this phenomenum.

Without doubt the physical structure of the milk powder particles is an important factor which must be taken into account.

A simple microscopic observation shows that particles of spray-dried whole milk are more or less spherical, have diameters ranging from 5 to 150 μm and often contain vacuoles, sometimes called air cells because they are usually filled with air at atmospheric pressure. Particles of pressure-dried whole milk often contain one more or less central vacuole, whereas particles of centrifugally dried whole milk generally contain a number of smaller vacuoles throughout the whole particle.

Fat globules and aircells are dispersed in a continuous phase which probably consists of amorphous lactose, milk salts and whey protein, usually called the milk serum material.

From photographs taken with an electron microscope Villanova and Ballarin (19) concluded that the size of fat globules in particles of spray-dried homogenized concentrated whole milk were smaller than 1 μm. On similar photographs published by other authors (16, 20) we measured diameters of 0.1 to 4 μm and 0.04 to 1 μm for powders from unhomogenized and homogenized concentrated milk, respectively.

As early as in 1922 the distribution of fat in dried milk particles was studied by microscopic methods (21, 22). Washburn (22) applied differential staining of fat and protein. He concluded from his observations that the fat in particles of roller-dried milk consists mainly of irregular patches on the surface of these particles, but that in particles of spray-dried whole milk the fat was present in the form of small fat globules, surrounded by a fat globule membrane.

The unusually good keeping quality of spray powders in comparance with roller-dried milk was ascribed to the presence of 'unbroken' fat globules in the spray powder particles. It is not surprising that Holm et al. (1) concluded a few years later from their experiments that free fat consisted of fat globules with damaged or broken membranes.

Lampitt and Bushill (23) showed that there are other possible explanations. These authors observed that the fat in roller-dried whole milk can be extracted almost quantitatively, whereas only a small part of the fat in spray-dried whole milk can be extracted under the same conditions. Three possible ways of explaining these differences were proposed:

a. Assuming that there is some protective sheath around the fat globules in liquid milk, such a sheath in the spray process is unbroken or reformed after the process of atomizing, acting as a protective layer when the milk is desiccated.

b. During the spraying process a protective film is formed on the surface of the fat globules with the result that these are not accessible to the action of fat solvents. Such a film is not produced in the roller process.

c. In the spray process the fat globules, either sheathed or not, are enclosed

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in a continuous mass of dried solids-not-fat, whilst in the case of roller process powder there is no such continuity of solids-not-fat and consequently solvent liquids can gain access to the fat.

Coulter and Jenness (24) assumed that the continuous phase of dried whole milk particles was impenetrable to fat solvents. However Choi et al. (25) doubted this because they found that by treating spray-dried whole milk with 96% ethanol only 5-8% of the lactose crystallized, whereas the fat could be extracted almost quantitatively. They suggested that the liberation of the milk fat may not be attributed to the lactose crystallization, but to coagulation of fat-globule protein membranes.

According to Lampitt and Bushill (23), who confirmed earlier observations (26), the fat in spray-dried whole milk becomes quantitatively extractable as soon as the lactose crystallizes due to water absorption.

King (11, 28) suggested later on that crystallization of the lactose provokes the development of a network of fine interstices and cracks along the sides and edges of the tiny crystals. This network pervading the particles makes them permeable towards gases and fat solvents. Indeed we were able to show (18) that the interior of particles of spray-dried whole milk is accessible to gases and liquids if the lactose has crystallized.

The physical structure of spray-dried whole milk was extensively studied by King (15, 27) using a fluorescence microscope and differential staining of fat and protein. In a review article in 1965 (28) he summarizes his conclusions as follows.

Fat in dried milk can occur either in a finely emulsified state or in a co-alesced de-emulsified state. In the latter case the membrane around the fat globules has been damaged or entirely removed, with the result that the globules are apt to flow together, to form 'pools' of fat. Such fat is extracted with fat solvents and was designated by Holm et al. (1) as 'free fat'. In a subsequent paper (29) he suggested that the unprotected fat permeates the dried milk particles and that part of it reaches the surface, rendering it water-repellent. This view of King was accepted by many authors.

Tamsma et al. (30) concluded from the increase in free fat with decreasing particle size of their foam dried milk, that free fat is present on the surface of particles, in accordance with earlier conclusions of King (15).

A correlation between surface areas and free-fat content of vacuum-foam-dried whole milk was also found by Berlin et al (31). These authors concluded that free fat appears in the form of small fat globules on the surface of the pow-der particles.

According to Mueller (16), who studied the physical structure of dried milk particles with an electron microscope, free fat is situated on the particle surface

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as patches or an irregular layer, especially at contact points between particles or in surface folds. A few years later we showed (17) that the free-fat content of spray-dried whole milk changes far more than the specific surface area, and in a subsequent paper (18) we therefore related the occurrence of free fat in dried milk to the presence of micropores in the particles.

In general the physical structure of dried milk particles as observed by electron microscopy (16, 20, 32) is similar to that observed by conventional microscopic methods (7, 11, 15). Amorphous lactose and other whey constituents are the continuous phase in which fat globules and casein micelles are dispersed. The latter have diameters ranging from 0.02 to 0.3 μm, but E.M. photographs obtained by Eggmann (32) of samples prepared by a freeze-drying technique show that the casein particles consist of sub-units with diameters of about 9 nm. During homogenization of the concentrated milk, some of the casein particles adhere to the fat globules and partly cover them.

Objections can be made to the methods of preparation of the slides or coupes applied by most authors (15, 16, 20, 21, 22, 27). In almost all cases water was used, which may cause changes in the physical structure of the particles. At this point we shall make a few other critical remarks.

1. As shown above most authors consider free fat as surface fat originating from unprotected fat globules or from globules with damaged membranes. As far as we know the consequences of this simple model have not been checked experimentally.

Mueller (16) did observe surface fat in particles of roller-dried milk, but his photographs show that it is only a small fraction of the total fat, whereas the fat can be extracted almost quantitatively.

If free fat is mainly surface fat, its content is likely to be proportional to the specific surface area of dried milk which has been disproved by our experiments (17).

Moreover the large difference in the free-fat content of spray powders prepared from homogenized and from unhomogenized concentrated milk cannot be explained satisfactorily by such a model. Mueller (16) concluded from his photographs that in both cases the amount of surface fat is low. We found that sometimes 80% of the fat in spray-dried milk can be extracted in 10 minutes, as will be shown later.

2. It seems rather unlikely that a dry fat globule membrane consisting for 50% of lipids with a thickness of 5–10 nm (16, 20, 33, 34) gives a better protection against fat solvents than non-fat dry milk solids with a more than tenfold thickness. Moreover Eggmann (32) concludes from his E.M. photographs that

fat globule membranes are never found in powder particles prepared from homogenized milk and very seldom in powder particles from unhomogenized whole milk. Other authors reported (16, 20) that they noticed membranes around fat globules, but we were not able to detect them in the published photographs.

If free fat consists mainly of unprotected fat globules, it has to be demonstrated how such globules inside the powder particles can be reached by fat solvents.

1.3 Effect of processing and storage conditions on the free-fat content of dry whole milk

Many workers have investigated the processing parameters which affect the free-fat content of dried whole milk.

Lampitt and Bushill (23) showed that the fat in whole milk powders prepared by a roller process can be extracted almost quantitatively by non-polar organic liquids in 20 hours at 20°C. Spray-dried whole milk had a much lower free-fat content when the same extraction method was applied (3 to 14% of the fat).

Blaauw (35) reported that centrifugally spray-dried whole milk contained considerably more free fat than pressure-dried whole milk from the same concentrated milk. The method of Lampitt and Bushill was used for the determination of the free-fat content. Foam-dried whole milk contained 50 to 90% free fat expressed as a percentage of the fat, according to Tamsma et al. (30). The extraction time was 30 minutes.

Hanrahan et al. (36) observed that the free-fat content of foam-dried powder strongly increased with the amount of nitrogen injected into the concentrated milk.

The free-fat content of freeze-dried whole milk was determined by Nickerson et al. (37) who used the Soxhlet extraction method and a contact time of 2 hours. These authors found that 40 to 90% of the fat could be extracted, with an average of 70%. Only a small portion of the lactose was crystalline.

Thus the amount of free fat in dried milk varies appreciably, depending upon the manufacturing method. It is usually low in spray-dried powders and high in roller-dried ones.

Reinke et al. (38) reported that large orifice nozzles (63/425) operated at pressures under 600 p.s.i. produced powders with relatively low (2.3%) free-fat values. When these nozzles were operated at 1000 p.s.i. the free-fat content increased to 6.9%. Dry solids content was 47%.

Blaauw (35) observed that the free-fat content of spray-dried whole milk, either centrifugally dried or pressure-dried, decreased considerably if the dry-

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solids content of the concentrated milk was increased from 35% to 50%.

Increased forewarming temperature or holding time of the fluid milk or both was conducive to an increased free-fat content of spray-dried whole milk, according to Reinke et al. (38). However Nickerson et al. (37) concluded from their results with freeze-dried whole milk that there was no significant correlation between the forewarming temperature and the free-fat content of the powder.

Experimental results obtained by Brunner et al. (39) indicated that the use of a low forewarming temperature (71°C), a low preheat treatment (57°C) of the condensed milk, low nozzle pressures (35–70 kg/cm²) and small orifice nozzles (69/20) in conjunction with low outlet temperatures in the drier, should produce a minimum amount of free fat.

Homogenization of concentrated milk prior to spray drying results in powders with much less free fat than is found in powders from unhomogenized concentrated milk as was shown by Holm et al. (1). This was confirmed by many other authors. According to a German patent (1968) spray-dried whole milk with less than 1% free fat can be obtained by very strong homogenization of the concentrated milk at 40 to 60°C.

Reinke et al. (38) remarked that homogenization of fluid milk did not result in significantly lower free-fat values.

Some homogenization may occur in normal processing, for example during concentrating in a long-tube vertical film evaporator, as was observed by Blaauw (35).

Storage conditions may be important for the free-fat content of milk powders. If the lactose crystallizes, due to moisture absorption from the surroundings, the free-fat content increases sharply. This may occur if milk powders are stored in paper bags in air with a high humidity.

Even if whole milk powders are stored in air-tight packages some change with time may take place. Litmann and Ashworth (12) observed that spray-dried whole milk stored for 3 weeks at 30°C contained more free fat than the same powder stored at 7°C during the same time. Reinke et al. (38) confirmed this observation but did not find a significant increase with time in contrast to the result of Brunner et al. (39). The latter authors noticed that powders with a relatively low initial free-fat content showed only a slight increase with time, whereas powders with a high initial free-fat content showed a considerable increase. No explanation was given.

As we pointed out earlier (17) the free-fat content of spray-dried whole milk is strongly influenced by particle size. Most of the authors mentioned above did not notice this connection. It is possible that many of the differences in the free-fat contents of these powders could be explained by taking into account

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the specific surface area. Particle size and particle shape may vary widely, depending upon the manufacturing method and drying conditions, such as viscosity of the concentrated milk, dry-solids content, nozzle size, spraying pressure or diameter and rotation speed of the disc. In a subsequent report we shall return to this subject.

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2. An evaluation of methods for the determination of free-fat content

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Abstract

Free fat in dried milk is usually defined as that part of the fat which can be extracted with organic solvents under standardized conditions. Unfortunately these conditions vary widely in the literature. Their influence is investigated in this paper. From the results the conclusion is drawn that the influence of the choice of the solvent and the mixing ratio of powder and solvent are of minor importance. Stirring the powder suspension appeared to increase the free-fat content considerably. This is ascribed to the powder particles being damaged by the stirrer, which makes the fat in the interior of the particle accessible to the solvent.

It is shown that the free-fat value of spray-dried whole milk depends not only on the contact time and extraction temperature, but also on the type of powder used. Spray powders prepared from homogenized concentrated milk showed a much smaller increase in free-fat content with time and temperature than did normal commercial whole milk powders.

Therefore results obtained by methods with different extraction times and temperatures are not comparable.

Because it was not clear which experimental conditions yielded free-fat contents relevant to other powder properties, two methods were usually applied, differing widely in contact time and extraction temperature.

2.1 Introduction

Free fat in dried milk is usually defined as that part of the fat which can be extracted with organic solvents under standardized conditions. However various workers have used widely differing conditions. Extraction times varied from 1 minute (1, 2) to 24 hours (3, 4, 5) and extraction temperatures, if mentioned, ranged from 20° to 70°C. The following organic solvents were used: diethyl ether (6), benzene (7, 8), petroleum ether (9, 10, 11, 12), carbon tetrachloride (3, 4, 12, 13, 14), carbon disulphide (15) and a mixture of petroleum ether and ethyl ether (16, 17, 18).

Naturally, data obtained by different authors are not comparable without considering their experimental conditions. Lampitt and Bushill (15) had already

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stressed in 1931 that the figures obtained by a Soxhlet extraction method were not comparable with those obtained by their standard method. This latter consisted of an extraction for 18 hours at room temperature of 2 g whole milk powder by 100 ml dried carbon disulphide in an Erlenmeyer flask. After filtration the fat in the filtrate was determined and expressed as a percentage of the powder. These authors found that results obtained with ethyl ether and carbon tetrachloride were equivalent to those obtained with carbon disulphide and that the free-fat content after a contact time of 15 days was equal to that found after 18 hours.

The method of Lampitt and Bushill has been widely applied (3, 4, 5, 21), but carbon tetrachloride was used instead of carbon disulphide. Tamsma et al. (14) also used this solvent but a contact time of 30 minutes was chosen, 'since the rate of extraction after 30 minutes was much less than in the region from 0 to 30 minutes shaking time'.

For practical reasons we introduced some years ago a method in which 10 g of powder were extracted for 10 minutes with 200 ml carbon tetrachloride at room temperature (12). The results were the sameif petroleum ether was used. Extraction time and temperature appeared to be important. Figures obtained with the above method were much lower in most cases than those obtained by a Soxhlet extraction with the same solvent.

In our opinion carbon tetrachloride is less suitable as a fat solvent because of its high density which causes powder particles to float on the surface.

Benzene was used by Lendrich (7) in 1924 and later on by Ritchie (8) who used a continuous extraction method. The latter found that the amount of extracted fat increased linearly with the logarithm of time.

Several authors used petroleum ether. Nickerson et al. (9) extracted their powders with this solvent for 2 hours in a Soxhlet apparatus, but did not publish further details. Pyne (11) applied the same method, but mentions 60–70°C as the boiling point of the petroleum ether. The influence of extraction time with this solvent was studied by van Kreveld and Verhoog (19). Their extraction temperature was probably about 50°C, for they used a Soxhlet extractor and petroleum ether with a low boiling point. They found that the free-fat content increased with time, but in many cases a fairly constant value was obtained after 7 hours. Consequently they introduced a 7-hours Soxhlet extraction with petroleum ether, as a standard method.

Very short extraction times were applied by Thomas et al. (16), who shook milk powder with a mixture of ether and petroleum ether and filtered through a sintered glass filter. Reinke et al. (18) used the same method. Only Lindquist and Brunner (17) mentioned a mixing ratio, namely 50 : 50.

Very short extraction times, e.g. 1–2 minutes are probably more theoretical

than real. The filtration of the powder suspension usually takes several minutes, unless adequate vacuum filtration is applied.

From the above the conclusion can be drawn that the free-fat value of dried whole milk may vary considerably with the experimental conditions. Although a few workers have paid attention to this problem, it has not been investigated systematically. This will be done in the following sections.

The free-fat content of whole milk powders is usually expressed as a percentage of the total fat, but some authors express it as a percentage (w/w) of the powder. One or the other method may be preferable depending upon the problem under consideration. If the influence of the free fat on the cream rising or foaming of reconstituted milk is studied, it can best be expressed as a percentage of total fat. If, however, the relation between free fat and other powder properties, such as the dispersibility or wettabillity, is investigated it might be better to express it as a percentage of the powder or as the free fat per unit of surface area. Actually we found that only a small part of the free fat in spray-dried whole milk is surface fat, as will be shown later.

As a rule we shall express free fat as a percentage of total fat but in a few cases we shall relate it to the weight of the powder.

2.2 The influence of experimental conditions on the free-fat value

For practical reasons we had to limit the number of variables and the number of powders. An investigation of the effect of the solvent, and of the extraction time and temperature on the free-fat value of powders with relatively high and low contents of free fat seemed indispensible. At first four samples were chosen from the powders available, viz two powders prepared in our pilot plant from homogenized concentrated milk (Samples 1 and 2) and two normal commercial whole milk powders (Samples 3 and 4).

Later on we inserted another commercial powder (Sample 5) because of its unusual high free-fat content. The pilot plant powders were the main and the cyclone fraction of the same batch of powder and were included in order to have two samples prepared from the same milk, but differing in particle size. The latter quantity was determined permeametrically as described in the next paper. It was found that the mean particle size of Sample 2 was half that of Sample 1. The commercial powders had particles of the same order of magnitude as the main fraction of the pilot plant powder, the mean particle size being 40 to 50 μm.

All powders were manufactured by pressure spray drying. The fat content ranged from 28 to 30 % and moisture content was 3.4 % or lower. No crystalline lactose was observed in the powder particles under the polarizing microscope.

In brief the experimental procedure for the determination of free fat was as follows. 2.50 g of powder were weighed in a 250-ml glass-stoppered Erlenmeyer flask and 100 ml solvent were added. During the first 10 minutes the suspension was shaken frequently by hand and thereafter every 15 minutes. If the extractions were extended to 20 hours, the shaking frequency was decreased to once per hour and the suspension was left overnight without agitation. If the extraction was carried out at temperatures differing from room temperature, the flasks were placed in a thermostatically controlled water bath. After the required extraction time the powder was filtered under vacuum through a sintered glass filter, Grade G.3. The clear filtrate was collected in a round-bottom flask and the solvent removed by distillation on a steam bath. The fat residue was then dried at 105°C for 1 hour and weighed. All determinations were carried out at least in duplicate. The difference between duplicate measurements was usually not more than 0.1 % of fat, but systematic errors may easily occur. Two errors are evident. First, the retention of solvent and thus a loss of dissolved fat in the powder and on the filter and glassware, which appeared to be 2.4%. This can be avoided by washing with an extra 25 ml petroleum ether. Because washing, in fact, is another short extraction with fresh solvent, this cannot be applied with short extraction times.

Lampitt and Bushill (15) eliminated this error by determining the fat in 50 ml filtrate and multiplying by a factor of 2, because the suspension was prepared with 100 ml solvent. However in this way a second systematic error was introduced. During filtration, about 3.0% of the solvent evaporates and then the fat concentration in the 50 ml filtrate is too high.

Therefore we usually estimated the fat residue in the total filtrate without washing on the filter. Since 2.4% of the extracted fat remains behind in the powder and the glassware, our results are low by that amount. The correction can be made if necessary, but in general this is not done, because only the relative free-fat content is relevant in most cases.

2.2.1 The effect of the fat solvent

Those organic solvents were chosen which were frequently used in the literature. These are benzene, carbon tetrachloride and two fractions of petroleum ether with boiling points of 50° and 68°C, respectively. Extractions were carried out with four powders and extraction times of 10 minutes and 2 hours at 22° and 40°C. The results are summarized in Table 1. We see that the differences between the results obtained with different solvents are small, although the figures obtained with benzene are significantly higher. This is in agreement with the conclusion of Lampitt and Bushill (15) who found that results obtained

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Table 1. The percentage of fat extracted from spray dried whole milk with four different solvents in 10 minutes and in 2 hours at 22°C and 40°C.

Sample No	Free-fat value (% of fat)							
	petroleum ether 50°C		petroleum ether 68°C		carbon tetrachloride		benzene	
	10 min	2 h	10 min	2 h	10 min	2 h	10 min	2 h
22°C								
1	1.6	1.7	1.7	1.9	1.6	1.7	1.9	1.9
2	9.9	10.1	9.8	10.3	9.9	10.1	10.1	10.4
3	8.0	9.4	7.6	9.0	8.0	8.7	8.3	9.3
4	9.1	10.0	8.7	10.1	9.1	10.0	9.8	10.8
40°C								
1	1.5	1.8	1.5	2.1	2.0	2.2	2.1	2.4
2	10.3	10.4	10.2	10.5	10.5	10.9	10.6	11.1
3	9.9	12.0	9.9	11.8	9.7	11.9	10.7	13.2
4	13.2	18.4	12.5	18.6	13.5	19.0	14.0	20.0

with carbon tetrachloride and ethyl ether were equal to those obtained with carbon disulphide.

Thus it is not important which fat solvent is chosen, at least in the range of extraction times and extraction temperatures we applied. Petroleum ether was used as a fat solvent for all the following determinations.

2.2.2 The influence of the way of agitating the powder suspension

Agitation refreshes the liquid layer on the particle surface and the way of agitation may therefore influence the amount of fat extracted. We performed some extractions at room temperature with and without stirring with the same powders and varying contact times. Stirring was carried out with a magnetic stirrer and a teflon-coated stirring bar. The rotation speed of the stirring bar was kept as low as possible, that is, all particles were just floating in the extraction liquid.

Extractions without stirring were performed as described in Section 2.2. The boiling point of the petroleum ether was 50°C.

The results shown in Table 2 clearly demonstrate that the free-fat content of spray-dried whole milk is considerably increased by stirring the suspension, particularly if the extraction time is extended to 30 minutes or more. Under the microscope we observed, in the same way as described earlier (20), that

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Table 2. The effect of the method of agitation of the powder suspension during extraction (22°C) on the free-fat value of spray-dried whole milk.
Sh = shaking by hand at stated intervals; M.S. = continuous magnetic stirring

Sample	Agitation	Free-fat value (% of fat)					
		1 min	10 min	30 min	2 h	10 h	20 h
1	Sh	1.5	1.6	1.4	1.7	—	1.8
	M.S.	2.3	2.3	6.5	13.4	42.5	66
2	Sh	9.5	9.9	10.0	10.1	—	10.3
	M.S.	10.1	10.1	15.2	22	45	63
3	Sh	6.5	8.0	8.6	9.4	—	9.8
	M.S.	6.9	7.8	14.5	29	45.5	74
4	Sh	7.2	9.1	10.0	10.0	—	10.8
	M.S.	7.4	9.2	13.3	21	49	74

after prolonged stirring all the vacuoles of the powder particles were filled with liquid whereas without stirring the vacuoles remained empty. It must therefore be assumed that stirring causes cracks in the powder particles, thus rendering the fat globules in the interior of the particles accessible to fat solvents.

The above results contrast with those of Lampitt and Bushill (15), who concluded from their experiments that stirring or shaking the suspension made no difference to the free-fat value of dried whole milk. Evidently the method of agitating the suspension can be important.

2.2.3 The influence of the mixing ratio

All experiments described in the preceding sections were carried out with 2.5 g powder in 100 ml extraction liquid. Other workers have applied very different ratios. Tamsma et al. (14) and Pyne (11) used 20 g in 100 ml, whereas Lampitt and Bushill (15) suspended 2 g in 100 ml solvent.

We investigated the influence of the mixing ratio as follows. Of two whole milk powders we suspended 2.5, 5.0 and 10.0 g each in 100 ml petroleum ether and extracted in the usual way for 2 hours at room temperature. By weighing we estimated that 0.6 ml solution was retained by 2.5 g powder on the filter and 3.0 ml by 10 g powder. Consequently we obtained free-fat values which were 2.4% lower when 10.0 g powder was used instead of 2.5 g powder. To avoid this error we washed the powder with 25 ml fresh solvent, which is permissible because the extraction time is very long compared with the contact time during washing. Evaporation of the solvent (3.0%) is not important if our procedure, described in Section 2.2, is applied.

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Table 3. Free-fat value of two whole milk powders determined by 2 hours extraction at 22°C and three mixing ratios.

Sample No	Free-fat value (% of fat)		
	2.5 g/100 ml	5.0 g/100 ml	10.0 g/100 ml
3	9.4	9.2	9.0
5	27.9	27.7	27.0

The results obtained in this way, as shown in Table 3, demonstrate that while the decrease of free-fat content with increasing amount of powder is significant, it is too small to be of practical importance. Thus the earlier published results obtained with different mixing ratios are comparable, provided the other experimental conditions were the same.

All further determinations were carried out with 2.5 g spray-dried whole milk in 100 ml solvent.

2.2.4 The effect of contact time and extraction temperature

As described in 2.1 extraction times varying from about 1 minute to 24 hours and extraction temperatures of 20–70°C have been reported. Several authors used a Soxhlet extractor and did not mention the extraction temperature. Litman and Ashworth (10) reported that their Soxhlet extractions were carried out at room temperature. We studied the temperature during Soxhlet extraction by placing thermocouples in the powder and found that the temperature was only a few degrees below the boiling point of the solvent e.g. if petroleum ether boiling point 50°C was used, the contact temperature turned out to be 44°C.

Thus the temperature mentioned by the above authors is not correct. The boiling point of the solvent used by Pyne (11) was 70°C, and consequently the contact temperature must have been 60° to 65°C.

In an earlier report (12) we showed that methods differing in contact time and extraction temperature yielded widely differing free-fat values. We therefore carried out a number of determinations with contact times varying from 10 seconds to 20 hours and extraction temperatures between 20° and 70°C. Under our conditions the filtration requires 5 seconds, so extraction times shorter than 10 seconds are not possible by this method. In the temperature range of 20° to 50°C we used petroleum ether with a boiling point of 50°C and above 50°C, petroleum ether with a boiling point of 68°C. No crystalline lactose was observed under the polarizing microscope in the powder residue after extraction.

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Table 4. The effect of extraction time and temperature on the free-fat value of spray-dried whole milk.
Solvents: petroleum ether, boiling points 50° and 68°C.

Sample No	Temp. (°C)	Free-fat value (% of fat)					
		10 sec	1 min	10 min	30 min	2 h	20 h
1	22	1.4	1.5	1.6	1.4	1.7	1.8
	40	—	1.6	1.5	1.6	1.8	2.5
	70	—	2.3	3.0	3.5	3.8	3.7
2	22	8.7	9.5	9.9	10.0	10.1	10.3
	40	—	10.0	10.0	10.0	10.0	10.1
	70	—	12.8	13.5	15	15	15
3	22	5.1	6.5	8.0	8.6	9.4	9.8
	40	—	7.8	9.9	11.1	12.0	14.2
	70	—	16.3	22	34	40	35
4	22	—	7.2	9.1	10.0	10.0	10.8
	40	—	9.2	13.2	14.9	18.4	25
	70	—	21	30	38	43	45
5	22	6.5	9.5	16.8	—	27	40
	40	—	12.0	19.4	—	36	59
	70	—	—	34	—	59	—
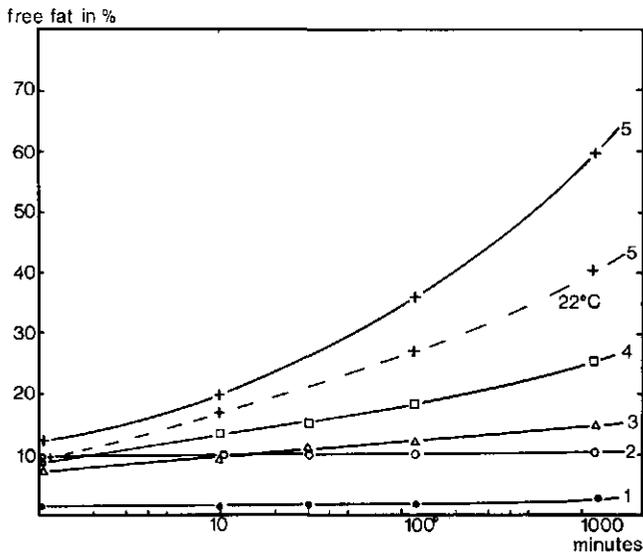
Fig. 1. Variation of free-fat value of spray-dried whole milk with extraction time at 40° and 22°C.

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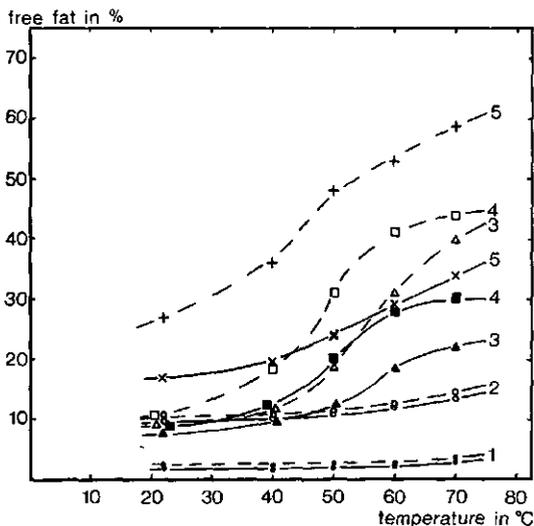
Fig. 2. Variation of free-fat value of spray-dried whole milk with temperature, using two extraction times; —— = 10 min; - - - = 2 hours.

From the results shown in Table 4 it can be concluded that the free-fat value of spray-dried whole milk may be considerably influenced by the contact time and extraction temperature. However this influence may depend largely on the type of powder. Spray powders prepared from homogenized concentrated milk show a much smaller increase in free-fat value with time and temperature than do similar powders from unhomogenized concentrated milk. This is illustrated in Fig. 1 and 2, which refer partly to the same results of Table 4.

Ritchie (8) concluded from his results with continuous extraction that there is a linear relation between the free-fat content and the logarithm of extraction time.

Fig. 1 shows that this is not true in all cases. Neither do we find that the major part of the free fat is extracted in the first five minutes as reported by Lampitt and Bushill (15) or in the first 30 minutes as reported by Tamsma et al. (14).

Results obtained by methods with different extraction times and temperatures are thus not comparable. There is no way of reconciling these results. A simple correction factor would not suffice because it would be different from powder to powder. Note, for instance, that the free-fat content of Samples 3 and 4 is lower than that of Sample 2 if extracted for 10 minutes or less at room temperature, but is higher if extracted for more than 10 minutes at 40°C or higher temperatures.

Because it was not clear which experimental conditions yield free-fat values of spray-dried whole milk which are relevant to other powder properties, we

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have for many years applied two methods, widely differing in contact time and extraction temperature. These are an extraction at room temperature for 10 minutes with petroleum ether and a 7-hour Soxhlet extraction with the same solvent. In the latter case the extraction temperature is about 44°C. Normally the results obtained with both methods on commercial spray-dried whole milk show considerable differences as we reported earlier (12), and will be shown in the subsequent papers.

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3. Particle size
Its estimation, influence of processing parameters and its relation to free-fat content

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Abstract

The free fat of dried milk was considered by many authors as surface fat on the powder particles. The specific surface area of powders is closely related to particle size, and we therefore investigated the influence of this factor on the free-fat content of spray-dried whole milk.

Particle size was determined by microscopic counting and by gas permeametry. Both methods are described, and it is shown that the choice of experimental conditions is important to obtain reliable results.

In contrast with the results of other workers we found that the particle size distribution of spray-dried milk can neither be described by a simple exponential law nor by a log-normal distribution. Mean particle size, calculated from the arithmetic mean of d^2 from countings, was compared with values obtained by a simple gas-permeameter. Good agreement was found if the shape factor was assumed to be 4.5, a value often found for spherical particles.

It is shown that particle density of spray powders increases with decreasing particle size.

In accordance with earlier results it was found that the mean particle size of spray milk powders decreases inversely with $\sqrt{p}$, p being the spray pressure. Orifice diameters appeared to be of minor importance. Increasing the dry-solids content of concentrated milk in the range of 30–45 % resulted in a reduction of the number of small particles. At 20 % d.s. the particle size distribution was different from that expected, probably due to the inclusion of air during droplet formation in the drier.

Finally the relation between fat content, moisture content and free-fat content of spray-dried whole milk was investigated. No influence of particle size on the fat content and the moisture content was found, but the free-fat content of the small particle fractions appeared to be much higher than that of the powder fractions which consisted mainly of the larger particles. It is suggested that the influence of some processing parameters on the free-fat content of spray-dried whole milk may be attributed to their influence on particle size.

3.1 Introduction

In a preceding report (1) we showed that many workers considered the free fat of dried whole milk as surface fat. As the surface area per gram of powder is closely related to particle size, we have paid some attention to the relation between particle size and free-fat content of such powders. A few results were

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published earlier (2), but the methods for the determination of particle size or specific surface area were not described in detail.

In the following, two methods, which we introduced some ten years ago in our laboratory and which are still applied, will be described. With these methods we studied the influence of certain process parameters on particle size, and the influence of particle size on the free-fat content of spray-dried milk.

3.2 Determination of particle size of spray-dried whole milk

Numerous techniques for the measurement of the size characteristics of powders have been developed, reviews of which are found in the literature (3, 4, 5, 6). Most of these techniques are unsatisfactory for normal spray-dried whole milk for one reason or another. Sieving is impossible because most particles are too small. Moreover they stick together, forming aggregates with larger apparent diameters. Sedimentation methods are not suitable because both particle size and particle density may vary widely within a powder sample (2). All techniques with liquids involve the difficulty of finding a liquid in which none of the milk constituents dissolves during the determination.

Various workers determined particle size of spray-dried whole milk by microscopic counting (7, 8, 9, 10, 11). Most of them gave no mathematical description of the size distribution. Only Hayashi et al. (8) mention a log-normal distribution.

Janzen et al. (11) concluded from a statistical analysis of their results that it is sufficient to count the size of all particles in ten fields of view under the microscope to obtain results which are representative for a powder sample. Such counting is very tedious and time-consuming, and is thus not applicable to routine measurements. Nevertheless the advantage of microscopic methods is the direct observation of particle size and particle shape.

During ten years of microscopic counting we found that acceptable results can be obtained with two fields each containing about 500 particles, if a few precautions are taken. This method is described below.

For routine measurements we developed a gas permeability method which gives the specific surface area. From the latter a mean particle size can be calculated if a few assumptions are made. The principle of this method, the experimental conditions which must be fulfilled and the simple apparatus we build will be described in the following, together with some results.

3.2.1 Microscopic counting

The main problem in microscopic counting is how to obtain a field of view

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under the microscope containing a number of particles with a size distribution which is representative of the particle size distribution of the powder. During the preparation of the slide segregation may very easily occur, giving rise to considerable errors. Reliable results can only be expected when considerable experience with the technique has been acquired. We use the following procedure.

Normally our powders were packed in 1–lb tins. The powder in the tin was thoroughly mixed with a spoon for some time. Segregation is not likely in sticky powders such as dried whole milk. With a small spatula two very small subsamples were taken from different parts of the tin and each suspended in a drop of paraffin oil on a slide. It is very important to prevent segregation during the preparation of the slide. While stirring the small particles may move to the edge of the preparation, which was also observed if a coverglass was applied. Therefore coverglasses have to be omitted.

Alternatively a preparation can be made by suspending a large powder sample in oil and transferring a drop of the suspension to a slide. But again during stirring, segregation can occur.

With a small magnification (50 ×) the preparations are observed under the microscope and two fields, each containing about 500 powder particles, are selected and photographed.

The fields were not selected at random as proposed by Janzen et al. (11), in that we omitted fields showing visible segregation. After development, the photographic plate is projected on a white plane with a magnification of 12 × and the particles are counted in size classes of 10 μm. Counting is facilitated by drawing a rectangular grid on the plate and by a home-built counter for registration of the results.

Normally particles of whole milk powders are almost spherical in shape but some may be somewhat elongated. For convenience we then measure only the maximum diameter. In the case of agglomerates the size of all primary particles is estimated separately as far as possible. Mean particle size is calculated simply by taking the arithmetic mean, but at low sizes we have to correct for the skew size distribution within the interval.

In a few cases the results of microscopic counting were compared with those obtained with a Coulter counter. Iso-propyl alcohol with 5% ammonium thiocyanate added, was used as a suspending medium. A few results are shown in Table 1. In our opinion the agreement between the countings of two fields from different slides is acceptable for most practical purposes. The rather good agreement between microscopic counting and Coulter counter measurements is remarkable, and is far better than found by Hayashi et al. (8) for skimmed milk powders using the same solution. Objections can be made to this solution

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Table 1. Particle size distributions of spray dried milk obtained by microscopic counting (M) and by a Coulter counter (CC).

Sample No	Percentage of particles in size interval (μm)											ΣN	Number of fields
	0–5	5–10	10–20	20–30	30–40	40–50	50–60	60–70	70–80	80–90	90–100		
1a M	10	48	25	9	4	2	1	—	—	—	—	663	1
1b M	10	45	26	9	7	3	—	—	—	—	—	670	1
2a M	7	27	27	17	11	6	2	2	1	—	—	495	1
2b M	5	23	27	16	15	6	3	2	2	—	1	547	1
3a M	38	29	16	8	5	3	1	—	—	—	—	620	1
3b M	37	32	15	5	5	2	2	1	1	—	—	434	1
4a M	0.7	38.3	33.5	13.5	6.1	3.7	1.7	1.1	0.8	0.5	0.2	1326	2
4b CC	—	35.6	34.7	14.6	6.7	3.8	1.8	2.0	0.4	0.1	0.1	4500	—
5a M	4.4	28.9	23.9	18.2	10.6	5.4	4.1	2.1	1.2	0.4	0.5	945	2
5b CC	—	21.8	25.6	28.1	13.2	6.1	2.2	1.3	1.0	1.0	0.1	3630	—

because part of the milk fat may dissolve and lactose crystallization may occur. Evidently this does not influence the particle size to a large extent in all cases.

Since several workers (3) have observed that many powders have a log-normal particle size distribution, it is natural to smooth an experimental size distribution by means of a plot on log-probability paper. However, according to our experience only in a few cases is a true log-normal distribution found. A plot of counting results of spray-dried whole milk often yielded the well known S-shaped curves. This is illustrated in Fig. 1.

On this occasion we counted more than 2000 particles of each sample to reduce statistical errors. Only one of the four curves is a straight line. Thus smoothing the counting results by means of a straight line on log-probability paper is not correct. Moreover the sensitivity of such a procedure is not sufficient at both ends of the distribution.

Heywood (12) showed that the number of particles dN falling within a small size range dx, may be related to the particle size x, by an equation of the form:

$$dN/dx = a.e^{-bx^n} \qquad (1)$$

Heywood calculated that theoretically the constant n can have any value between 0 and 4 for many real powders.
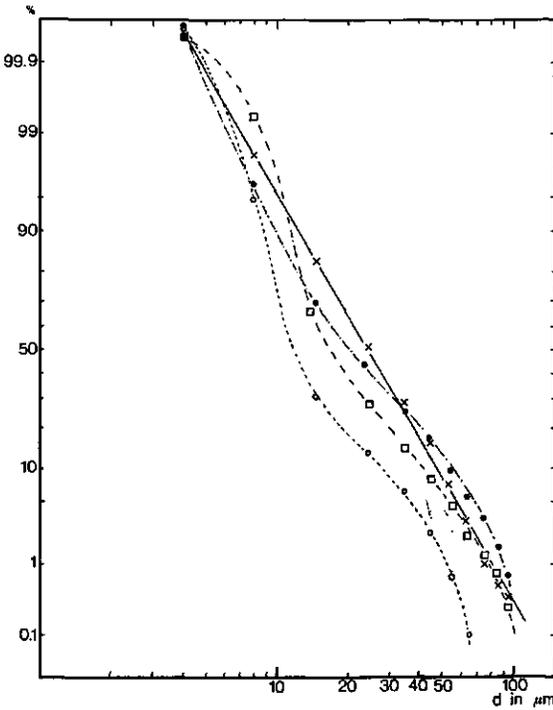
Fig. 1. Particle size distribution of spray-dried whole milk obtained from microscopic countings plotted on log-normal probability paper.

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Martin et al. (13) indicated earlier that for a powder which had not been subjected to a grading process n equalled 1. We also obtained in some cases a straight line if log dN/dx was plotted against the particle diameter x. This is shown in Fig. 2. In other cases, however, we observed that only part of the distribution obeyed an exponential law and that the agreement was better as the powder particles became smaller. Fig. 3 illustrates this observation.

Thus, since both the log-normal distribution and the exponential power law fail, and as no other law has been proposed, no smoothing of statistical fluctuations is possible. The only way of obtaining a mean particle size is to calculate the arithmetic average from the counting results without a correction. How this mean value corresponds with that determined by gas permeametry is shown in the next section.

3.2.2 Mean particle size from specific surface area

The mean particle size of powders can be calculated from their specific surface areas as determined by the rate of flow of a gas through a column of packed
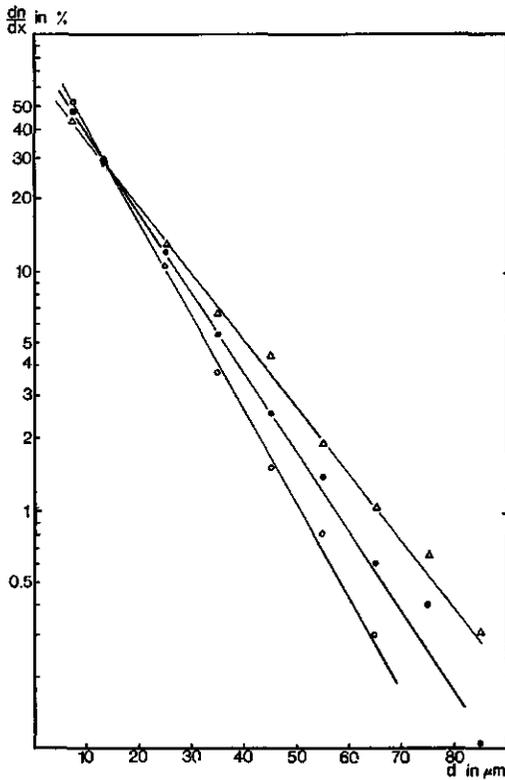
Fig. 2. Particle size distribution of spray-dried whole milk from microscopic countings plotted on log-linear paper.
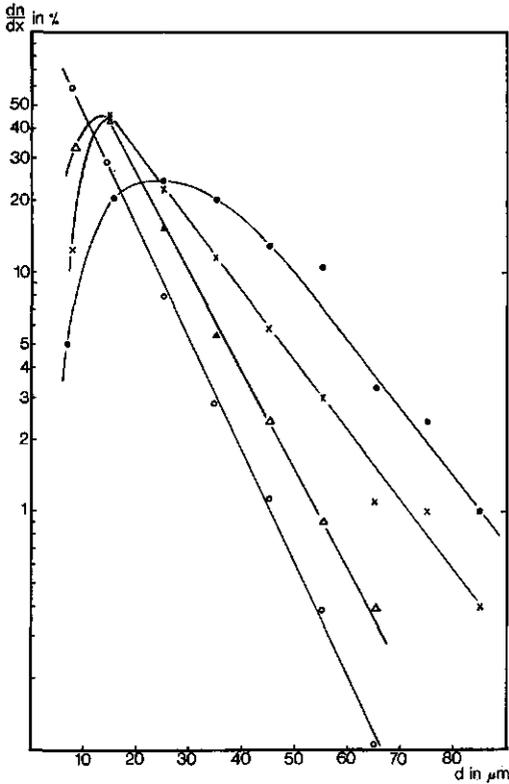
Fig. 3. Particle size distributions of spray-dried whole milks with different mean particle size. ○ d̄ = 12 μm; △ d̄ = 17 μm; x d̄ = 24 μm; ● d̄ = 34 μm.

particles. This gas permeability technique, originally suggested by Carman (17) and independently by Dalla Valle (15) is now widely used in powder technology because of its rapidity and the relatively simple apparatus required. A review of theory and practice in this field is given by Orr and Dalla Valle (4).

Early investigations showed that the flow of the fluids through packings is governed by Darcy's law:

$$\frac{V}{t} = P \cdot \frac{A}{\eta} \cdot \frac{\triangle p}{L} \tag{2}$$

$\triangle p$ is the pressure drop across a powder bed with a length L and a cross-sectional area A, $\frac{V}{t}$ is the volume of fluid flowing through the packing in t seconds, η is the viscosity of the fluid, and P the permeability of the powderbed.

P can easily be obtained from equation (2) by measuring the flow rate of gas through a packing of known dimensions applying a known pressure drop $\triangle p$.

The basis of interpretation of permeability data in terms of powder charac-

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teristics is the Hagen-Poiseuille equation for laminar flow of fluids through a cylindrical capillary.

Kozeny (16) assumed that a particulate bed behaves as a bundle of interlocking capillaries of irregular shape and derived the following equation for the permeability:

$$P = \frac{1}{k \cdot S_v^2} \cdot \frac{e^3}{(1 - e)^2} \tag{3}$$

S_v = the volume specific surface area of the particles; k = the Kozeny constant or shape factor; e = the porosity of the particle bed.

The porosity e, defined as the void volume divided by the total volume of the packing, can be obtained from:

$$e = 1 - \frac{\varrho}{\varrho'} \tag{4}$$

ϱ = the packing density of the powder bed; ϱ' = the particle density.

In the case of spray powders only a mean particle density is relevant, and this can be estimated by gas displacement techniques.

The Kozeny constant k is empirical in nature and has been evaluated on the basis of experimental evidence by Carman et al. (4). For spherical particles k was often found to be about 4.5 (18). As particles of milk spray-dried by pressure are more or less spherical, we always used 4.5. Recently Fox et al. (17) published an indirect method for deriving appropriate k values for milk powders. They obtained strongly diverging results for different types of milk powders, e.g. $k = 2.94$ for regular spray-dried commercial skim milk and 4.88 for their pilot-plant dried milk.

If a powder consists of spherical particles, the mean partical size can be obtained from the specific surface area by means of the equation:

$$\bar{d}_s = \frac{6}{S_v} \tag{5}$$

The evaluation of the specific surface area by means of the Kozeny-Carman equation, being the combination of equations (2) and (3), from porous bed dimensions, the fluid rate and the pressure drop across the powder bed, involves tedious arithmetic calculations. This can be greatly simplified by adopting standardized conditions and calibrated charts.

3.2.2.1 Apparatus and experimental procedures. Many years ago a simple permeameter, similar to those described earlier (18, 19), was constructed. It yielded satisfactory results and is still in use for routine measurements. The

principle is shown schematically in Fig. 4. A cylindrical perspex tube with a nylon screen at the bottom is filled with a powder column of 10.0 cm length and connected to the tube system by a rubber stopper. Compressed air, dried with silica gel is fed into the tube system. The pressure drop across the powder sample can be adjusted by a needle valve to a standard value which can be read from water filled U-tube. The flow rate of the air through the packing can be read from one of the four flow meters (Brooks Co.) inserted in the system. The sample tube can easily be exchanged with other tubes of different internal diameters if necessary. The flow meters are checked periodically by replacing the sample tube by an ordinary calibrated soap film meter. The appearance of the instrument is shown in Fig. 5.

Preparation of the powder bed is carried out by filling the sample tube with a known weight of powder and compressing it to the required length of 10.0 cm by tapping the tube on the table. Uniform packing can be facilitated by an aluminum weight on top of the powder bed while tapping. Packing density can be varied by changing the weight of the powder sample.

Free-flowing powders such as spray-dried skim milk can easily be packed in this way to the required porosity, but difficulties arise with the more cohesive whole milk powders, due to channel formation in the powder bed. For this reason we added 0.7% of a free-flowing agent to whole milk powders. This addition appeared to have a negligible influence on the surface area of such powders, as will be shown later.

Mean particle density is determined by means of a Beckmann air comparison pycnometer, which we described earlier (20).

For routine measurements the experimental conditions were standardized as much as possible. Of the four sample tubes with cross-sectional areas of 0.95, 3.20, 7.28 and 12.84 cm², the tube with A = 3.20 cm² gives the best results in our apparatus, as judged from the plot of the permeability P against the porosity function $e^3/(1 - e)^2$ being a straight line in accordance with the Kozeny-Carman equation.
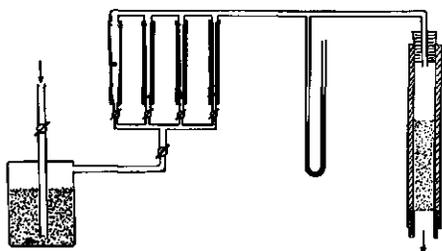
Fig. 4. Schematic diagram of the permeameter.
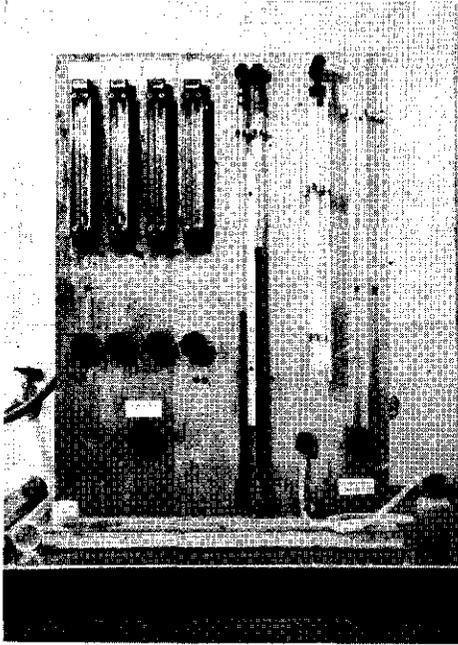
Fig. 5. The permeameter.

In the same way we found that the pressure drop across the powder column with a length of 10.0 cm should not exceed 10.0 cm water and the packing density should be 0.60 to 0.70 g/cm³. Deviations were often observed if the pressure drop was higher and the packing density was lower. This is illustrated in Fig. 6 with a relatively fine (1) and a relatively coarse (2) skim milk spray powder. Probably channelling is the cause of this phenomenon.

Using these results we constructed charts for the instrument by means of which the specific surface area of spray-dried milk can easily be obtained under standardized conditions. One of the charts is shown in Fig. 7. Viscosity of the air was assumed to be 180.10^{-6} poises at 20°C, according to the Handbook of Chemistry and Physics.

3.2.2.2 Results. A few results are shown in Fig. 8. From the slope of the lines $k.s_v^2$ can be estimated and thus the mean particle diameter d_s; k is assumed to be 4.5. The permeametric results for spray-dried milk were checked by comparing the mean particle diameters d_s with those calculated from microscopic countings. In the latter case the mean particle size d_m was calculated by averaging d^2 to make it comparable to d_s which is a 'surface diameter'. Some results are given in Table 2. Specific surface areas of the main (a) and of the

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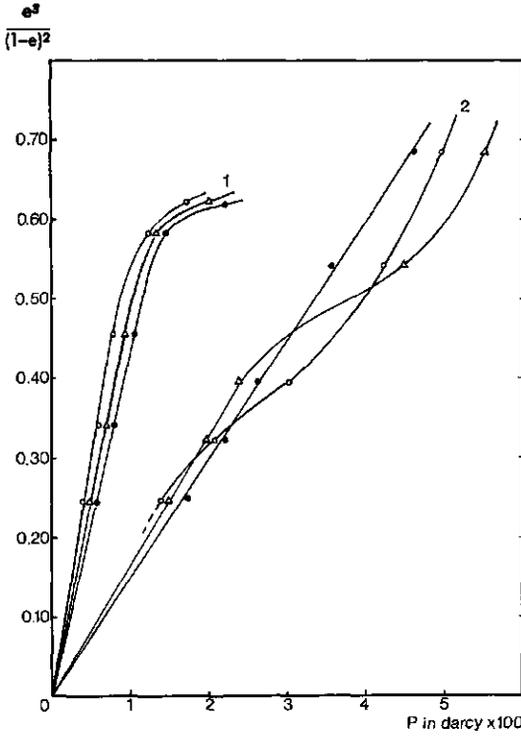
Fig. 6. Permeability of packed columns of spray-dried whole milk in relation to the porosity function $e^3/(1-e)^2$. L = 10 cm; A = 3.20 cm²; ● Δp = 10 cm; △ Δp = 20 cm; ○ Δp = 30 cm.
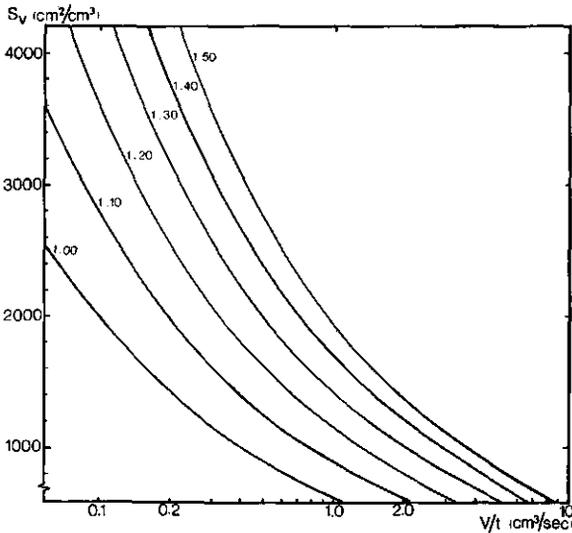
L   = 10 cm
A   = 3.20 cm²
Δp = 10 cm
ϱ = 0.65 g/cm²
temperature = 20°C

Fig. 7. Example of a calibrated chart for the determination of the specific surface area of spray-dried milk. The figures near the curves indicate the mean particle density ϱ.

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$\dfrac{e^3}{(1-e)^2}$

0.90

0.80

0.70

0.60

0.50

0.40

0.30

0.20

0.10

A B C D

0   1   2   3   4   5   6   7   8

P in darcy × 100
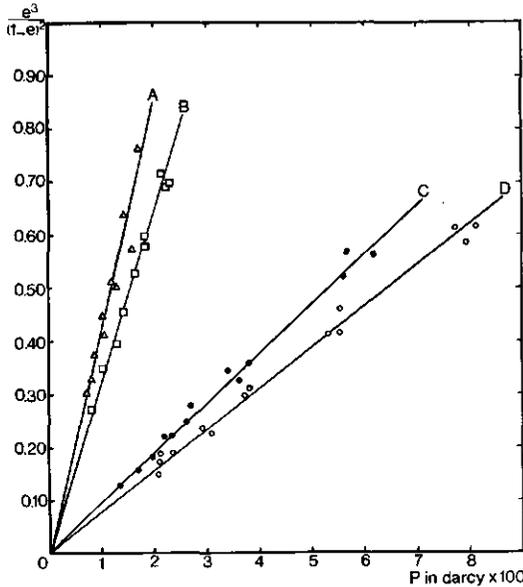
Fig. 8. Results obtained with permeameter and standard powder bed dimensions and pressure drop. L = 10 cm; A = 3.20 cm²; Δp = 10 cm; temperature 20°C.

cyclone fractions (b) of five skim milk powders manufactured in our pilot plant spray drier were estimated in triplicate for two packing densities. Mean values of the six determinations are shown. The standard deviation of the mean d_s was 2% or less in most cases as compared to 5% or less for the standard deviation of d_m, estimated from duplicate countings.

Table 2 shows that in spite of the assumptions made, the agreement between the results of the two methods is good in most cases.

Table 2. Mean particle size of spray dried skim milk determined by microscopic counting d_m and by gas permeametry d_s. S_v = specific surface area in cm²/cm³. ϱ' = particle density in g/cm³

Sample	ϱ'	S_v	$d_s(\mu m)$	$d_m(\mu m)$
Da	1.10	1650	36	36
Db	1.24	3230	19	19
Ea	1.21	1550	39	40
Eb	1.33⁵	2930	20	17
Fa	1.13	1570	38	37
Fb	1.27	3200	19	17
Ha	1.13⁵	1270	47	44
Hb	1.30	2630	23	17
Ka	1.10	1280	47	50
Kb	1.32⁵	2900	21	17

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Long series of measurements showed that generally the value of d_s is slightly higher than that of d_m for fine powders powders such as the cyclone fractions of our powders. Possibly a correction of the Kozeny-Carman equation for the so-called Knudsen or molecular flow is necessary for more accurate results. With relatively coarse powders deviations sometimes occur, d_m being up to 10% larger than d_s. Probably streamline conditions are not fulfilled, thus invalidating equation (3).

As mentioned before we add 0.7% fina silica (Neosyl-Crossfield Chemicals) as a free-flowing agent to cohesive whole milk powders to prevent channel formation in the powder bed.

This addition of a large number of very fine particles might increase the specific surface area but the effect is small as can be concluded from Table 3. Probably the fine silica particles adhere to the surface of the larger milk powder particles and the streamline flow of gas through the powder bed is not materially disturbed by them.

Thus it would appear that the results of gas permeametry are acceptable for the routine control of mean particle size of spray-dried milk.

3.3 Particle density in relation to particle size

In earlier work we concluded that the density of small particles in a sample of milk spray-dried by pressure is considerably higher than that of the larger ones in the same powder. This conclusion was based on two observations.

First we found that the cyclone fractions of spray powders prepared in our pilot plant drier have a mean particle size which is smaller by a factor two than that of the corresponding main fractions (2) whereas the mean particle density is usually 10–20% higher (20). The figures shown in Table 2 are in good agreement with these earlier data.

Table 3. The influence of the addition of 0.7% Neosyl[1] to spray powders on the mean particle size (μm) found by gas permeametry.

Sample No	Spray powder	d_s in μm	
		—	0.7% Neosyl
1	skim milk	54	52
2	skim milk	35	34
3	whole milk	59	60
4	whole milk	46	40

[1] Neosyl = fine silica (Crosfield Chemicals).

Secondly we observed microscopically that when a spray powder sample is suspended in a liquid with a suitable density and centrifuged 10 minutes at 1000 r.p.m. in a Gerber-type centrifuge, the upper layer always contains relatively large particles, whereas the sediment mainly consists of the smaller powder particles (2).

In the meantime we carried out some further investigations with two spray skim milk powders. Samples of these powders were suspended in carbon tetrachloride-liquid paraffin mixtures of varying density and centrifuged for 10 minutes as above.

The sediment was transferred to a slide and the particle size distribution was determined as usual by microscope. Mean values of the duplicate measurements are shown in Table 4.

Evidently the relative volume of the vacuoles in small spray powder particles is smaller than in the larger particles of the same powder. In many of the smallest particles vacuoles are absent as can easily be observed under the microscope.

This phenomenon can only be understood in terms of droplet formation and the drying mechanism of droplets. Although much work has been done on these subjects (e.g. 21) a complete description has not yet been given.

The observation that the vacuoles in spray powder particles are not immediately filled with air of atmospheric pressure (20) indicates that the 'case hardening' of the drying particles is the main cause of vacuole formation, at least in particles produced by pressure spray drying.

A second indication is that the mean particle density of such powders can

Table 4. Particle size distribution (%) of skim milk powder fractions with different particle densities ϱ'.

Size class (μm)	Powder I		Powder II		
	$\varrho' > 1.024$	$\varrho' > 1.218$	$\varrho' > 1.024$	$\varrho' > 1.195$	$\varrho' > 1.218$
0–5	4	22	2	6	12
5–10	10	30	21	29	40
10–20	12	16	19	21	19
20–30	16	11	20	12	10
30–40	10	5	15	9	6
40–50	10	9	9	6	5
50–60	8	3	5	5	2
60–70	9	2	4	4	3
70–80	10	1	3	3	1
80–90	5	—	1	2	1
90–100	5	—	1	1	—
>100	1	—	—	—	—

be increased by lowering the air temperature in the drier, thus decreasing the drying rate of the particles.

As in fact case hardening is caused by the difference in drying rate of the outer shell and the interior of the particles, it is likely that the 'case hardening effect' will increase with particle diameter. The higher density of small spray powder particles can thus be explained.

3.4 The influence of drying parameters on the particle size of spray-dried whole milk

In dairy practice it is important to know how the particle size of whole milk powders depends on the process variables, especially the drying conditions. Several authors paid attention to this problem (7, 9, 22, 23). Manus and Ashworth (9) concluded from their experiments that increasing the degree of pre-concentration from 20 to 40% total solids resulted in whole milk powder not only of greater density but with a higher percentage of the larger-size particles. A similar conclusion was drawn by Blaauw (7) from experiments with concentrated milk containing 35 and 50% of dry solids. Tracy et al. (23) studied the influence of spray pressure on the particle size distribution of whole milk, but they changed the nozzle type simultaneously. These authors found that the particles became larger with increasing nozzle size and decreasing spray pressure. Hayashi et al. (8) studied the particle size of non-fat dry milk by microscopic counting, sieving and Coulter-counter methods. They concluded that particle size was not significantly effected by inlet air temperature and preheat treatment, but an increase of total solids (30–50%) or a decrease of pump pressure (245–106 kg/cm²) increased particle size.

We studied the influence of spraying pressure, nozzle size and dry solids content of the concentrated milk on particle size of dried whole milk. In all cases one parameter was varied at a time, starting from the following standard conditions: pre-concentration 40% solids, nozzle 64/21 (Spraying Systems Co.); pump pressure 100 kg/cm².

We varied each of the variables as follows: pre-concentration from 20 to 45%, nozzle from 74/20 to 58/21; pressure from 60 to 200 kg/cm².

The pre-heating temperature was invariably 72°C and the outlet temperature of the drier 85°C in all cases.

Since Larcombe (24) found a linear dependence of $\bar{d}$ on $1/\sqrt{p}$, p being the pump pressure, we plotted in Fig. 9 mean particle size, obtained from microscopic counting, against $1/\sqrt{p}$. A straight line was in fact obtained, in agreement with the observation of Larcombe. Thus the particle size of spray-dried whole milk is considerably influenced by the spraying pressure.

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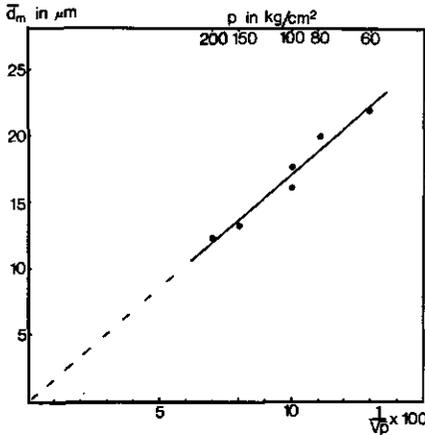
Fig. 9. Relationship between mean particle size and pump pressure of spray-dried whole milk.

On the other hand particle size distribution proved to be practically independent of the choice of the pressure nozzles in the range we used as shown in Table 5. Finally, in agreement with previous reports (7, 8, 9) the dry-solids content of the concentrated milk influences particle size, as can be concluded from Table 6. In the range of 30–45 % dry solids, the number of particles < 10 μm decreases from 60 % at 30 % dry solids to 47 % at 45 % dry solids.

An exception is the powder from milk with 20 % dry matter.

It is true that the fraction of particles < 5 μm is very high, but at the same time many large particles are present. Also the latter contain more and larger vacuoles than usually found in such particles. We believe that in this case a different mechanism for vacuole formation is prevailing, namely the inclusion of air during droplet formation at the nozzle. Possibly the relatively low viscosity of the concentrated milk promoted this phenomenon. It is clear that this air inclusion may have a considerable effect on the particle size distribution.

Table 5. Mean particle size (μm) of whole milk powders pressure spray-dried with nozzles of different orifice diameter. (The numbers refer to the notation of Spraying System Co.) Dry-solids content of the concentrated milk 40 %. Spray pressure 100 kg/cm².

Mean particle size (μm)

Nozzle 74/20	69/21	64/21	60/21	58/21
17.1	16.2	16.2	18.2	17.7
—	—	17.4	—	—
—	—	17.7	—	—

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Table 6. Particle size distributions of whole milk powders prepared by pressure spray drying of concentrated milk with different dry-solids content. Spray pressure 100 kg/cm²; nozzle 64/21 (Spraying Systems Co.)

Size class (μm)	Number percentage of particles in size class					
	20%	30%	35%	40%	45%	dry solids
0–5	23	5	3	5	5	
5–10	28	55	51	46	42	
10–20	20	29	28	26	28	
20–30	11	6	10	11	12	
30–40	9	2	4	5	6	
40–50	4	1	3	3	3	
50–60	2	1	1	3	2	
60–70	1	—	—	1	2	
70–80	1	—	—	1	1	
80–90	—	—	—	—	—	
90–100	—	—	—	—	—	
Mean value	16.5	12.3	14.5	16.2	16.5	
Viscosity 20°C (in c.p.)	4	17	35	140	360	

3.5 Particle size and free-fat content of spray-dried whole milk

In a previous paper (2) we reported that small particles in a powder sample of 500 mg contained much more free fat than the larger ones in the same sample, but it was assumed that the fat content was independent of particle size. This conclusion was based on the qualitative microscopical observation that the smallest particles have the highest density. This was quantitatively confirmed in Section 3.3.

Further on we demonstrated with a few examples that the free-fat content of the cyclone fractions of spray-dried whole milk was considerably higher than that of the corresponding main fractions, the latter having half the specific surface area of the former. Some other investigations were also carried out on this subject.

A series of milk powders with fat contents ranging from 20 to 60 % in the dry solids was prepared in the pilot plant drier. At each fat content the concentrated milk, with a dry-solids content of 40 %, was divided into two parts. One part was homogenized at a pressure of 250 kg/cm² with a Rannie homogenizer prior to spray drying. The other part was not homogenized. The two portions were then dried in a Rogers-type drier under the following conditions: pressure 60–80 kg/cm², nozzle 66/21 and outlet temperature 80–90°C. The cyclone fractions of the powders were collected separately. In this way we

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obtained four powders with different particle size and free-fat content from the same concentrated milk.

In a few other cases the concentrated milk was divided into four equal parts. Two of these were treated as above, the other two were spray-dried by a centrifugal process. We thus obtained eight powders from the same concentrated milk. The powders were used for several other experiments which will be described later.

Fat contents of the powders were determined with the Mojonnier modification of the Röse-Gottlieb method. Moisture contents were estimated by weighing before and after drying for 20 minutes in vacuo at 100 to 105°C. Free-fat contents were determined by two methods, viz a 10 minutes extraction at room temperature and a 7 hours extraction with a Soxhlet apparatus (44°C). Specific surface areas were measured as described above.

The results obtained with 16 powders prepared from three lots of concentrated milk are shown in Table 7. The powders manufactured from homogenized milk are marked H and the main fractions and cyclone fractions are marked a and b, respectively.

Table 7 shows that the fat content is independent of particle size. Although we usually find that the moisture content of the cyclone fractions is slightly lower than that of the corresponding main fractions, this cannot be concluded from the figures in Table 7.

Particle size, however, is very important for the free-fat content of both powder prepared by pressure spray drying and by centrifugal drying (samples C15 and C16). The small particle fractions b contain 6 to 10 times as much free fat as the corresponding main fractions a, which agrees with earlier results (2).

If the free fat is considered to be situated as a layer or as patches on the surface of the powder particles, as was done by many authors, the amount of free fat per unit of surface area must be 3 to 5 times as high on the surface of small particles as on larger ones in the same powder. This would seem rather unlikely.

Moreover we found that sometimes 60 to 80 % of the fat can be extracted in 10 minutes, and it is not likely that all of this fat is located on the particle surface. In earlier reports (2,20) we suggested that the free fat of spray-dried whole milk consists, at least partly, of those fat globules inside the powder particles which can be reached in some way by fat solvents.

In agreement with the results shown in the preceding report, homogenization of the concentrated milk before spray drying decreases the free-fat content considerably, and the percentage of free fat is not influenced to any large extent by the extraction time and temperature, in contrast with that of powders prepared from unhomogenized milk.

In our opinion the physical structure of the powder particles is influenced

Table 7. Fat content, moisture content and free-fat content of spray-dried whole milk in relation to particle size as characterized by the specific surface area S_v.

Sample No	S_v (cm^2/cm^3)	Fat content	Moisture content	Free-fat content	
				10 min, 22°C	7 h, 44°C
11a	1440	25.7	1.9	3.1	13.0
11b	2730	25.7	1.8	34	44
12a H	1430	25.7	1.7	1.5	1.5
12b H	2520	25.7	1.5	7.1	7.4
13a	1240	30.3	1.2	8.7	47
13b	2500	30.0	1.7	61	74
14a H	1170	29.7	2.7	1.1	1.3
14b H	2360	29.8	2.0	6.1	6.7
C 15a	1130	29.9	2.0	10.4	33
C 15b	2880	29.8	1.7	79	79
C 16a H	1000	30.1	1.5	1.0	1.1
C 16b H	2000	30.1	1.7	6.6	6.7
17a	1150	35.5	1.8	8.4	59
17b	2390	35.2	2.2	73	84
18a H	1020	34.9	3.3	1.9	1.9
18b H	2180	35.2	2.7	10.0	12.2

by homogenization as well as by the particle size. We will return to this subject in a subsequent report.

Several workers (1) related the free-fat content of spray-dried whole milk to processing conditions, such as the dry-solids content of the concentrated milk, nozzle size and spraying pressure. Both increasing the dry solids and decreasing the pump pressure reduced the free-fat content. This can easily be explained by the increasing particle size resulting from these changes, as shown in 3.4. Thus in this particular case the influence of process parameters on the free-fat content of spray-dried whole milk can be explained by taking particle size into account.

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4. Significance of free fat for other properties of practical importance

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Abstract

A high free-fat content of spray-dried whole milk is often considered to be a disadvantage because it may have an effect on some other properties which are of practical importance. With 20 powders widely differing in free-fat content, several experiments were carried out to verify the relationship between free fat and other properties reported in the literature. In contrast with earlier investigations, other factors were eliminated as far as possible by preparing 4 or 8 powders from the same batch of concentrated milk. The free-fat content was varied by homogenizing part of the concentrated whole milk and by collecting powder fractions of differing particle size.

From the results the following conclusions were drawn:
1. There is no influence of the free fat on the development of oxidation flavour during 6 months' storage at 30°C in the presence of air;
2. The solubility of spray-dried whole milk is usually better if its free-fat content is higher, but probably there is no causal relationship between the two quantities;
3. Below a free-fat content of 20% (of the fat) there is a tendency for the dispersibility to increase with decreasing amount of free fat. This is not the case above 20% free fat. Because both particle size and homogenization may effect dispersibility as well as free-fat content, no causal influence of free fat on dispersibility could be observed.
4. Neither cream rising nor foam formation during reconstitution is materially influenced by the amount of free fat in the powder. Churning of the butterfat by vigorously stirring during reconstitution was observed only with powders containing much free fat, prepared from unhomogenized concentrated milk. No quantitative correlation was observed between the amount of churned butterfat and free-fat content of the powder.

4.1 Introduction

A high free-fat content of dried whole milk is generally considered to be a disadvantage. The background is that several authors reported correlations between the free-fat content of dried milk and other properties of practical importance, which have been summarized in an earlier report (1) as follows:
a. The development of oxidation flavour during storage;
b. The dispersibility or wettability during reconstitution;

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c. The rising of cream and foaming or scum formation in the reconstituted milk;

d. The stickiness of dried whole milk.

In addition, the soaking of paper bags by the fat observed with roller-dried whole milk and not with spray dried whole milk was attributed to the presence of a high percentage of easily extractable fat in roller dried milk (2). We carried out a few experiments at 22°C with spray dried whole milk on brown paper under a pressure of 2 kg/cm² and did not observe soaking of the paper even if the free-fat content of the powder was 80 %.

In the present report the influence of the free-fat content on the properties mentioned under a, b and c has been studied, but its influence on the stickiness of spray-dried whole milk will be treated in the next paper.

We limited our experiments to spray-dried whole milk. In earlier investigations no attention was paid to other factors which may influence the free-fat content in addition to the powder properties mentioned above. It would be ideal to have available a number of powders only differing in free-fat content. This is not possible in practice. The best compromise we found was to prepare a number of powders with various free-fat contents from the same concentrated milk. Free-fat content was varied by homogenizing part of the concentrated milk prior to spray drying and by collecting powder fractions of different particle size, viz the main and cyclone fractions. In this way 4 or 8 different powders can be obtained from the same batch of concentrated milk. Details were described in Section 5 of the paper No. 3 in this series (3).

Powder samples prepared from homogenized milk are marked with H, powders prepared by a centrifugal process are marked with C, and the main and cycloon fractions, differing by a factor 2 in particle size, are marked with a and b, respectively.

In addition, we sometimes used a few normal commercial whole milk spray powders (No 3, 4 and 5) and pilot plant powders No 1 and 2.

Two methods were applied to determine the free-fat content of the powders, because it was not clear which experimental conditions would yield free-fat contents relevant to other powder properties. They were:

a. An extraction at room temperature during 10 min with petroleum ether;

b. A 7-hours Soxhlet extraction with the same solvent (44°C). Both methods have been discussed earlier (4).

4.2 Free fat and the development of oxidation flavour during storage

In 1925 Holm et al. (5) concluded that though definite proof was lacking, their results indicated that the presence of larger quantities of free fat tend to in-

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crease the susceptibility of the fat to oxidation and thus to impair the keeping quality of dried milk. Their reasoning was as follows: with increased fat content of the spray powders, the free fat content showed a sudden increase and at the same time the keeping quality showed a sudden decrease at approximately the same fat content (24%). These results were in direct contradiction to those earlier obtained by Supplee (6), who found a progressive improvement of keeping quality if the fat content was increased from 5 to 55%.

The oxidation flavour is often called tallowiness but for convenience we prefer to use the first term.

Shipstead (7) reported in 1952 that during storage of spray-dried whole milk the free fat on the particle surface oxidized first, while the dense mass of non-fat dry solids protected the interior fat.

A few years later Verhoog (8) found that whole milk powders with extremely high free-fat contents showed no accelerated deterioration after 3 months storage at room temperature.

Greenbank and Pallansch (9) concluded from their results with foam spray-dried whole milk that the free glycerides, equivalent to the 'classic free fat' and the free lipids, began to oxidize 2-4 weeks before the total glycerides and lipids. Kontson et al. (10) reported that the peroxide content of fat isolated from foam spray dried milk was similar to that of vacuum dried milk foam, and referring to earlier results of Kliman et al. (11) concluded that it is improbable that this fat oxidation can be detected organoleptically.

Finally Ritchie (12) concluded that, although the extractable fat had a slightly higher peroxide number than the other fat in dried whole milk, there is no indication that the free-fat oxidizes more rapidly during storage.

Because of the above contradictory results, we carried out some measurements with whole milk powders varying both in fat and in free-fat content. Immediately after production the powders were packed in 1-1b tins under nitrogen and stored at 20°C.

The experimental procedure was as follows. After opening the tins a sample was taken from each tin for a flavour test. The powder remaining in the tins was stored for 24 hours at room temperature in a relatively dry place (20°C and 40% R.H.) and was stirred from time to time, with a spoon to replace the nitrogen in and between the powder particles by dry air. Thereafter the tins were closed and stored at 30°C. This temperature was chosen because it had often been observed that under these circumstances the development of oxidation flavour can be noticed in normal commercial spray-dried milk after 3 months. Test samples were taken from the tins after 1, 2, 3 and 6 months storage.

The tests were carried out in accordance with the regulations of the Dutch Dairy Control Office (ZKB), by a panel consisting of four experienced persons,

Table 1. Development of oxidation flavour during storage at 30°C in spray-dried whole milk with various amounts of free fat as determined by two different methods.

Sample No	Fat (%)	Moisture (%)	Free fat (%)		Mean taste scores				
			10 min 22°C	7 h 44°C	fresh	1m	2m	3m	6m
11a	25.7	1.9	3.1	13.0	6.7	6.8	6.3	6.5	6.6
11b	25.7	1.8	34	44	6.8	6.6	6.3	6.6	6.4
12aH	25.7	1.7	1.5	1.5	6.9	6.8	6.8	6.6	6.5
12bH	25.7	1.5	7.1	7.4	6.8	6.5	6.9	6.4	6.6
13a	30.3	1.2	8.7	47	6.9	6.7	6.5	6.5	6.4
13b	30.0	1.7	61	74	6.8	5.9	6.2	6.0	6.1
14aH	29.7	2.7	1.1	1.3	6.8	6.7	6.6	6.5	6.5
14bH	29.8	2.0	6.1	6.7	6.8	6.4	6.3	6.1	6.5
C15a	29.9	2.0	10.4	33	6.9	6.5	6.5	6.2	6.4
C15b	29.8	1.7	79	79	6.6	5.8	6.1	5.8	6.3
C16aH	30.1	1.5	1.0	1.1	6.8	6.5	6.2	5.9	6.3
C16bH	30.1	1.7	6.6	6.7	6.7	6.2	6.3	6.0	6.2
17a	35.5	1.8	8.4	59	6.9	6.7	6.4	6.6	6.4
17b	35.2	2.2	73	84	6.3	6.3	6.2	6.3	6.1
18aH	34.9	3.3	1.9	2.0	6.8	6.8	6.6	6.5	6.1
18bH	35.2	2.7	10.0	12.3	6.9	6.6	6.6	6.5	6.2
Average					6.78	6.46	6.42	6.31	6.37

but the figures were assessed in a slightly different way. Powders without any defect were marked with 7. If a slight oxidation flavour was observed, a mark 6 was given, indicating that the taste was just satisfactory. An unsatisfactory or bad taste was marked with 5 and 4, respectively. Whereas the ZKB expresses the taste in whole units, we do it in quarters to obtain somewhat more differentiation. The standard error of the mean of four persons was usually found to be 0.1 point.

The results are shown in Table 1. With one exception (17b) the taste score of the fresh samples was similar. All powders show a deterioration with time as usual, although considerable fluctuations occur. In general, the taste of the milk from large particle fractions is slightly better than that of the corresponding small particle fractions containing much more free fat.

Apart from this there is no correlation between oxidation flavour and free-fat content, which is illustrated by Fig. 1 which shows the mean taste scores of the powders after 3 months' storage in relation to free-fat content determined by the short extraction method. A similar conclusion holds for results obtained with the long extraction method.
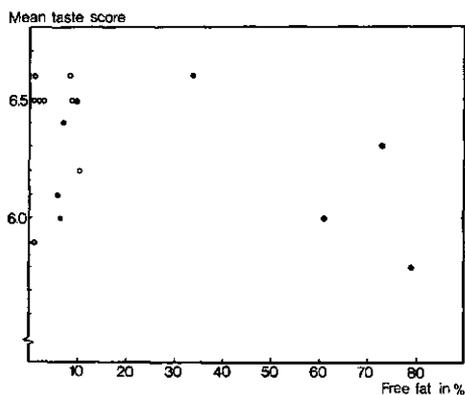
Fig. 1. Mean taste scores of spray-dried whole milk after 3 months storage at 30°C in relation to the free-fat content. ○ main fractions; ● cyclone fractions.

Conclusion: in our experiments with spray-dried whole milk, varying considerably in free-fat content, the free-fat content was found to have no effect on the development of oxidation flavour during storage at 30°C in the presence of air.

4.3 Reconstitutability of spray-dried whole milk in relation to its free-fat content

4.3.1 Review of the literature

It is well known that the reconstitution of milk powders with water to a liquid milk is rather difficult. The reconstitution involves a complex of factors which contribute to the ease and completeness of the dispersion and solution of a powder.

Numerous methods have been proposed to characterize such a process, a review of which has been given by King (13). This worker divided them into six categories, which are the determination of:
- the wettability of the powder particles
- the self-dispersion
- the sinkability
- the dispersibility
- the speed of dissolution of the power particles
- the solubility after a predetermined contact time.

Most of the above quantities differ fundamentally, but it is difficult to observe them separately by experiment. For the earlier methods we refer to King's review, and shall only discuss results which are relevant to our investigation.

Many workers have reported that the fat content of spray-dried whole milk affects the wettability, the sinkability, the self dispersion and the dispersibility

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(13). However, Ashworth (14) found that the effect of the fat content on the wettability was small with powders containing 12, 25 and 34% fat, all powders giving high wettability values. On the contrary this author mentioned a fairly close inverse correlation between wettability and free-fat content. Lateron this was confirmed by Mol and de Vries (15).

Pyne (16) determined the wettability of milk powders by measuring the contact angle between a water drop and a tablet of compressed powder. It was observed that the contact angle at room temperature increased linearly with the percentage volume of fat in the powder. This author reasoned that the composition of the particle surface was the same as that of the particle interior, and thus there is no evidence of extensive fat migration or the formation of a layer of free fat coating the particle surface, as suggested by King (13).

From microscopic observations it was concluded by Mohr (17) that a high free-fat content resulted in a poor wettability, preventing the powder particles from dissolving rapidly.

Nickerson et al. (18) concluded that although the wettability and dispersibility characteristics of freeze-dried skim milk were excellent, the presence of free fat in freeze-dried whole milk powder decreased the rate of wetting and, as a result, such powders did not reconstitute as readily in cold water as did the spray-dried powders. Data obtained by Tamsma et al. (19) with foam-dried milk showed that the dispersibility decreased only slightly with increased free-fat content. Hanrahan et al. (20) found with the same type of powders that the free-fat content as well as the dispersibility increased with the nitrogen injection rate.

In 1966 Samhammer (21) concluded from his experimental results that the solubility of dried whole milk is better if the free-fat content is lower, but the speed of solution was not influenced by the free-fat content. If, however, the free fat was removed from the powder by a 2-hours extraction with diethyl ether, the wettability was improved, but the solubility remained unchanged. In another report (22) this author mentions that the free fat did not influence the solubility of non-instant milk powders but it decreased the wettability and increased the dispersibility of instant powders. A moderate free-fat content was considered an advantage because the solubility was better, although the wettability was somewhat lower.

King (13) attributed the poor wettability of spray-dried whole milk to the presence of unprotected fat permeating the particles and as part of it reaches the surface this is rendered water-repellent.

The above short review of literatuie shows that the influence of free fat in milk powders on reconstitution properties is still open to discussion because of contradictory results. They may have been caused by other interfering factors. For example, attention was seldom paid to the influence of particle size on the

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reconstitution properties, at least in the case of spray-dried whole milk. On the contrary several authors (13, 16, 23, 24) reported that the wettability of non-fat dry milk increased considerably with increasing particle size.

We carried out some measurements with groups of powders varying in free-fat content, but prepared from the same concentrated milk, thus eliminating a number of possible influence factors. Powders with different particle size were included to vary free-fat content as well as to investigate the influence of particle size. Reconstitution properties are characterized by the solubility and the dispersibility with moderate agitation. These quantities were chosen because they were felt to be most relevant to household practice.

4.3.2 Experimental procedures

Many methods have been proposed (13) for the determination of dispersibility and solubility. They all have their advantages and disadvantages. We estimated the solubility of the powders according to the method of the Dutch Dairy Control Office (ZKB) because this is normal practice in the Netherlands. In brief the procedure is as follows. Depending on the fat content of the powder a weight of about 30 g is dissolved in 200 ml water of 60°C. After shaking for 10 minutes, part of the milk is transferred to a centrifuge tube and centrifuged in a Gerber-type centrifuge. The sediment volume is a measure for the solubility.

A disadvantage of this method is that undissolved particles floating on the surface are not taken into account. We therefore also applied the CCF solubility test proposed by van Kreveld and Verhoog (25). These authors determined the undissolved-solids content of the upper layer (x) as well as of the bottom layer (y) of the reconstituted milk. The milk was prepared by sprinkling 30 g of powder on 225 g of water both of 20°C and stirring with a spoon for 3 minutes. Lumps of powder were crushed against the wall of the beaker. The contents of the beaker were transferred to a separatory funnel and held at room temperature for 30 minutes before the upper and bottom layer were separated. For practical purposes the sum of x and y (being the amount of undissolved powder in the top and bottom fraction) was considered to be a good measure of the solubility of the powder.

Dispersibility was determined by Eisses who uses the ADMI method for skim milk powders with a few modifications. These are a shorter mixing time and a slightly different mixer. The procedure is as follows: 52 g of dried whole milk are dispersed in 400 ml water at 24°C by stirring for 10 seconds in a Hobart Kitchen mixer. The contents of the mixing beaker are then filtered rapidly through a 0.210 mm screen and the dry solids content of the filtrate is determined.

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Results obtained with 18 pilot plant powders and 2 commercial powders which varied considerably in free-fat content are shown in Table 2.

4.3.3 Discussion of the results

4.3.3.1 Solubility. Table 2 shows that all powders fall within the ZKB limit for whole milk powder of extra quality, i.e. less than 0.3 ml sediment. Van Kreveld and Verhoog (25) proposed the following scale for their x and y values:

$$x + y \leq 1.0 \quad \text{very good solubility}$$
$$1.0 < x + y \leq 2.0 \quad \text{good solubility}$$
$$2.0 < x + y \leq 3.0 \quad \text{moderate solubility}$$
$$3.0 < x + y \quad \text{poor solubility.}$$

According to this scale powder samples No 3, C16a and 18a have a poor solubility, which conclusion does not agree, however, with the ZKB test. Such a disagreement is often observed, probably because the ZKB test only accounts for those undissolved particles which go into the sediment as discussed above, and the temperature of reconstitution is different.

Further, the accuracy of the two methods must be taken into account. The standard deviation in the results of the ZKB test varies with the sediment volume, being 0.05 at 0.2 ml and 0.1 at 0.3 ml. With a few exceptions the duplicate results of the CCF test differed by 0.1 or less.

Considering the results in Table 2, it is striking that the poor solubility of Samples 3, 16a, 16b, 17a and 18a is due to undissolved particles in the top layer X. Only with Samples C 16a and C 16b can this be understood easily, because the average particle density was equal to or lower than the density of the surrounding liquid. The mean particle density of the other powders is considerably higher. Probably the high density components of these particles, viz the lactose and milk salts, dissolved very quickly, thus leaving behind slowly dispersing powder particles, mainly consisting of fat, casein and probably enclosed air, with a density lower than that of the dispersing liquid.

Now it is clear why the ZKB test is not a good measure for the solubility of spray-dried whole milk, because only the sediment is taken into account. It is therefore not surprising that no correlation can be observed between solubility and free-fat content of the powders.

While the ZKB test shows no correlation with free-fat content, the CCF test does so in a remarkable way: the powders with the worst solubility have the lowest free-fat content with both long and short extraction.

A more close examination of the results in Table 2 shows that:

1. The solubility (CCF test) of the small particle cyclone fractions containing

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Table 2. Solubility and dispersibility of spray-dried whole milk with various amounts of free fat (% of fat).

Sample No	Fat (%)	Moisture (%)	Particle density (g/cm³)	Free fat (%)		ZKB test	CCF-test			Dispersibility		
				10 min 22°C	7 h 44°C		X	Y	X + Y	1	2	mean
1	30.6	1.7	1.14	1.6	2.4	0.09	0.8	0.8	1.6	63	—	63
2	30.6	1.4	1.21	9.9	11.2	0.09	0.1	0.2	0.3	47	47	47
3	28.1	2.7	1.18	8.0	18.5	0.30	3.5	0.1	3.6	55	—	55
4	27.9	3.4	1.20	9.1	—	—	—	—	—	53	—	53
11a	25.7	1.9	1.13	3.1	13.0	0.08	0.7	−0.1	0.6	70	66	68
11b	25.7	1.8	1.23	34	44	0.10	0.2	0.1	0.3	45	41	43
12aH	25.7	1.7	1.12	1.5	1.5	0.09	0.1	0.2	0.3	91	83	87
12bH	25.7	1.5	1.21	7.1	7.4	0.08	0.2	0.2	0.2	68	63	66
13a	30.3	1.2	1.11	8.7	47	0.07	0.4	−0.1	0.3	67	58	63
13b	30.0	1.7	1.25	61	74	0.08	0	0.1	0.1	48	43	45
14aH	29.7	2.7	1.14	1.1	1.3	0.07	0.6	1.4	2.1	88	85	86
14bH	29.8	2.0	1.21	6.1	6.7	0.16	0.2	0.5	0.7	69	60	65
C15a	29.9	2.0	0.90	10.4	33	0.04	0	−0.3	−0.3	72	68	70
C15b	29.8	1.7	1.07	79	79	0.04	0.6	−0.4	0.2	43	38	41
C16aH	30.1	1.5	0.91	1.0	1.1	0.25	4.7	0.4	5.1	76	72	74
C16bH	30.1	1.7	1.01	6.6	6.7	0.28	1.9	−0.1	1.8	50	49	50
17a	35.5	1.8	1.10	8.4	59	0.08	1.4	−0.2	1.2	57	65	61
17b	35.1	2.2	1.23	73	84	0.07	0.5	−0.1	0.4	48	46	47
18aH	34.9	3.3	1.13	1.9	2.0	0.06	3.5	2.5	6.0	69	70	70
18bH	35.2	2.7	1.18	10.0	12.3	0.06	0.4	0.8	1.2	56	53	55

relatively much free fat is better than the corresponding main fractions with a lower free-fat content;

2. Powders from homogenized concentrated milk contain less free fat and are at the same time less soluble than powders of comparable particle size from the same concentrated milk which was not homogenized. A statistical analysis show that the above differences are significant at the 1 % level, according to Wilcoxons matched pairs signed ranks test (26).

In the strict sense it cannot be concluded that there is a relationship between free-fat content and solubility of spray-dried whole milk, because two factors interfere, viz particle size and homogenization. In our opinion a high free-fat content is not the cause of the good solubility but only a phenomenon occurring simultaneously. With the CCF solubility test, the powder suspension is stirred for 3 min and thus small particles with a high dissolution rate contribute to a high solubility. In fact the speed of dissolution is determined with this test.

As the specific surface area and thus the contact area between water and particle surface of the cyclone fractions is twice that of the corresponding main fractions (27), their initial speed of dissolution must also be twice as high. Probably their 6–10 times higher free-fat content is less important than the speed of dissolution.

It is well known that the homogenization of milk causes several changes (28, 38). Not only is the fat globule size reduced, but the surface layer of the new fat globules is different from that of the original ones. On the other hand little is known about the changes that take place when concentrated whole milk is homogenized either by a homogenizer or in the pressure nozzle during spray drying. Eggmann (29) observed that casein particles consist of subunits with diameters of about 9 nm which partly cover the fat globule surface during homogenization. These partially coated fat globules were observed with an electron microscope in powder particles prepared from homogenized milk. It is not impossible that such a coating gives the fat globules a better projection against fat solvents, if in fact it does actually cover them.

Homogenization of the concentrated milk decreases both the free-fat content and the particle porosity as will be shown in a subsequent paper. Because the particle porosity influences the penetration rate of liquids into the powder particles, it may greatly affect both the free-fat content and the initial rate of dissolution of the powder particles.

As far as we know, particle size and homogenization are the most important factors which affect the free-fat content in normal dairy practice. Therefore it must be stated that the solubility of spray-dried whole milk is usually better as its free-fat content increases. This conclusion is in agreement with that of Samhammer (22).

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Conclusion: the solubility of spray-dried whole milk usually improves as its free-fat content increases, but probably there is no causal relationship between these quantities. Particle size and homogenization of the concentrated milk may be more important than free-fat content.

4.3.3.2 Dispersibility

Originally the ADMI method (30) was developed for instant non-fat dry milk. If this method is applied to normal spray-dried whole milk, almost all commercial powders have a good dispersibility, contrary to normal household practice.

If, however, the stirring time is decreased from 30 seconds to 10 seconds, as proposed by Eisses (31), considerable differences in dispersibility are found as shown in Table 2, which agrees well with visual observation. For instance, powder samples No. 12a and 14a with a dispersibility of about 90%, while of poor solubility, were qualified as fairly good instant powders when dissolved in water of 20°C by stirring with a spoon for 3 minutes. If on the other hand the dispersibility was 40–50% according to the Eisses test, such powders were considered to be non-instant.

The time interval between duplicate measurements of the dispersibility was about 4 weeks. We therefore give the results of both series of determinations in Table 2.

From these results it can be concluded that the dispersibility of the cyclone fractions is much lower than that of the corresponding main fractions. The cause may be the higher free-fat content as well as the lower particle size. In agreement with other workers (13, 23, 24) we found that the dispersibility of the small particle cyclone fractions of spray-dried skim milk was much lower than that of the corresponding main fractions. Free fat cannot have influenced the dispersibility of such powders and so particle size must be an important factor.

In Fig. 2 we plotted the dispersibility of our powders against their free-fat contents (10 min and 22°C) expressed as a percentage of the powders. From this graph it can be concluded that, if the free-fat content is 6% or more, the dispersibility is independent of it. But, in spite of the large spread, there is a tendency for the dispersibility to decrease with increasing free-fat content at lower values. When comparing the dispersibility of powders of approximately the same particle size, it turns out that powders from homogenized concentrated milk have higher dispersibilities than powders from the same non-homogenized concentrated milk. The difference is significant at a level of 2.5%. For the rest, there appears to be no direct effect of the free-fat content on the dispersibility. Both particle size and homogenization of the concentrated milk

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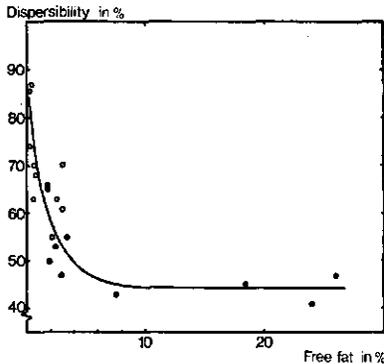
Fig. 2. Dispersibility of spray-dried whole milk in relation to its free-fat content expressed as a percentage of the powder. ○ main fractions; ● cyclone fractions.

may affect the dispersibility more than does the free-fat content.

It may expected that the properties of the particle surface, e.g. the wettability, influences the dispersibility and the fat content per unit surface area may be an important factor. It is as yet unknown which part of the free fat is surface fat and how the surface fat is distributed on the particle surface. Pyne (16) concluded that the composition of the particle surface was the same as that of the particle interior, while we found (3) that the free-fat content calculated on a basis of surface area was 2–5 times as high in cyclone powders than in the corresponding main fractions. This indicates that only part of the free fat is located on the particle surface because the fat content of both powder fractions is equal (Table 2).

More extensive research on this subject will be necessary to solve this problem.

Conclusion: if the free-fat content of spray-dried whole milk was 20 % (of the fat) or higher, no effect of the free fat on the dispersibility was observed. Below this value there is a tendency for the dispersibility to increase with decreasing free fat content. Dispersibility of powders of approximately the same average particle size is considerably increased by homogenizing the concentrated milk. Because both particle size and homogenization may affect dispersibility as well as free-fat content, no direct effect could be found of the free fat on dispersibility.

4.4 Surface conditions of whole milk reconstituted from powders with various percentages of free fat

4.4.1 Review of the literature

It is well known that on reconstituting roller-dried whole milk, large fat lenses appear on the milk, which is not the case with normal commercial spray pow-

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ders. King (32) related this phenomenon to 'unprotected' fat globules rising from the interior of the milk to the surface, forming clumps of globules, lenses and spots of fat.

Tamsma et al. (19), on the contrary, reported that no correlation could be observed between the speed of cream separation during centrifuging of reconstituted milk and the amount of free fat in their foam-dried milk samples.

Extensive experiments with spray-dried whole milk varying in free-fat from 3–44 %, carried out by Verhoog (8), showed no effect of the free fat on the speed of formation of fat lenses on the surface of the reconstituted milk.

Formation of surface scum during reconstitution of milk was related to the amount of free fat in the powder by Litman et al. (33, 34). They postulated that this defect is due to a fat-protein complex involving free fat and unstable protein. An analysis of the scum yielded an average composition of 48 % fat and 34 % protein.

King (35, 36) observed microscopically that foam or scum on reconstituted milk contained numerous clusters of fat globules and protein particles. This worker also concluded that the formation of a fat film on glassware and fat lenses on the surface of the milk was correlated with a high free-fat content of the milk powder.

We investigated the 20 powders used in the preceding sections but added a powder with a high content of crystalline lactose: 1k. This was powder sample No 1 which had been allowed to absorb moisture from humid air until severe lactose crystallization was observed under the polarizing microscope.

4.4.2 Experimental procedures

Foam or scum formation and the rising of cream in reconstituted milk made from powders with varying free-fat content were studied simultaneously as follows: 20 g powder were dispersed in 140 g water of 50°C by stirring for 30 seconds with a Kitchen mixer (Inventum 3-mix, 760 rpm). During the stirring the 400-ml beaker was rotated by hand to disperse the powder as well as possible in the liquid.

Immediately after stirring, the milk was transferred to a measuring cylinder and the volume V_0 of the milk including scum or foam was noted. This was repeated after standing for 5 minutes at room temperature: V_5. The volume difference $V_0 - V_5$ is a measure of the stability of the foam, if present.

The above determinations comprise both foam and scum, the latter being foam with undispersed powder material.

In a few cases the reproducibility of the first reading was bad as a result of very unstable foam. Many foam lamellae collapsed in these cases during the

transferance of the milk to the measuring cylinder.

After the second volume reading the milk was returned to the 400-ml beaker and allowed to stand at room temperature for $1\frac{1}{2}$ hours. Intermittently the milk was stirred with a rod to promote the solution of still undissolved powder particles.

The milk was then again transferred to a dry 250-ml measuring cylinder and left undisturbed for 16 hours (i.e. overnight) at room temperature. The next morning the upper 30 ml of the milk were removed by sucking and the fat content estimated. The ratio between the observed fat content of the top layer (g_t) and that of the milk as a whole (g_c) is a measure of the rising of the cream (C_r) which we shall express as the excess of fat in the top layer:

$C_r = (g_t/g_c - 1)\ 100\%$.

Usually the inaccuracy in the duplicate measurements of g_t/g_c was smaller

Table 3. Foam development, cream rise (C_r) and churning in reconstituted whole milk from powders with various free-fat contents.

Sample number	Fat %	Free fat (% of total fat)		Rising of cream		Foam volume(%)		Churned fat (% of fat)
		10 min 22°C	7 h 44°C	g_t/g_c	C_r %	$t = 0$	$t = 5$ min	
1	30.6	1.6	2.4	1.00	0	70	10	
2	30.6	9.9	—	0.97	0	10	2	
3	28.1	8.0	18.5	1.00	0	40	2	
5	27.8	9.5	50	1.09	10	80	2	
11a	25.7	3.1	13.0	1.09	10	3	3	0
11b	25.7	34	44	1.11	10	3	3	0.8
12aH	25.7	1.5	1.5	1.01	0	160	150	0
12bH	25.7	7.1	7.4	0.99	0	150	30	0
13a	30.3	8.7	47	1.16	15	60	2	3.5
13b	30.0	61	74	1.15	15	40	2	3.6
14aH	29.7	1.1	1.3	1.01	0	50	40	0
14bH	29.8	6.1	6.7	1.00	0	60	30	0
C15a	29.9	10.4	33	1.34	30	20	3	6.5
C15b	29.8	79	79	1.51	50	120	4	9.4
C16aH	30.1	1.0	1.1	1.01	0	120	110	0
C16bH	30.1	6.6	6.7	0.99	0	140	120	0
17a	35.5	8.4	59	1.26	30	140	10	2.1
17b	35.2	73	84	1.44	40	120	4	3.4
18aH	34.9	1.9	2.0	1.01	0	60	50	0
18bH	35.2	10.0	12.3	0.99	0	90	60	0
1k	30.6	84	—	0.60	—40	6	3	

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than 5%. Visual observations after 16 hours showed that a ratio of $g_t/g_c = 1.10$ had hardly any practical importance, because only if g_t/g_c exceeded 1.15 was a visible cream layer present on the reconstituted milk. We therefore rounded C_r off to 5%.

After a long standing time the volume of the milk without foam turned out to be 160 ml. We express the volume of foam or scum V_f relative to this volume:

$$V_f = \left(\frac{V_0 - 160}{160}\right) 100\%.$$

During the preparation of this paper our attention was drawn by Glas et al. (37) to a correlation they observed between the amount of free fat in milk powders as found by Soxhlet extraction and the amount of churned butterfat on the surface of the milk. They prepared their milk by dissolving 30 g of powder in 200 ml water of 40°C by vigorously stirring for 2 minutes with a high-speed Philips mixer (HM 3000). After standing for 5 minutes the surface was judged visually.

This led us to carry out a few similar experiments with a number of powders which were still available in closed tins and packed under nitrogen. The experiments were performed in the same way as those of Glas et al., except that we tried to estimate the amount of churned butterfat quantitatively by filtering with a 0.1 mm stainless steel screen. No churned butterfat was observed on the surface of the filtrate, so we assumed that we had removed all churned butterfat in this way. The residue on the screen was washed twice with water and then dissolved in 200 ml petroleum ether. After filtering off the filtrate was transferred to a round bottom flask and the petroleum ether evaporated. The weight of the fat residue obtained, expressed as a percentage of the fat in 30 g powder is shown in Table 3 together with the other results.

4.4.3 Results and discussion

Table 3 shows that the rising of cream in milk from powders prepared from homogenized concentrated milk is negligible. This was to be expected in view of the small fat globule size. A free-fat content of 10% or more does not influence the rising of cream in milk of such powders.

Although a high free-fat content, especially the Soxhlet free-fat content, tends to favour cream rising within the group of powders prepared from non-homogenized concentrated milk no quantitative relationship between free-fat content and cream rising can be observed. Particle size is not important for the rising of cream, because the long standing time and the relatively high water temperature must have led to complete solution of the powder particles. Pro-

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bably the cream rising is caused by the relatively large number of large fat globules present in the milk of such powders, as will be shown later.

It is remarkable that the cream rise in milk from samples C 15a and C 15b, prepared by a centrifugal process, is significantly higher than in milk from Samples 13a and 13b prepared from the same concentrated milk by pressure drying. Probably the reduction of fat globule size during droplet formation is higher with a pressure nozzle than with a spinning disk.

Table 3 further shows that the fat globule size in milk powders affects the stability of the foam formed during reconstitution. Scum was not observed notwithstanding the short stirring time. Reconstituting powders from homogenized concentrated milk yielded much foam with a high stability, whereas powders from non-homogenized concentrated milk gave little or very unstable foam.

Since it is well known (38) that the temperature may greatly influence the foaming of milk, we also carried out a few determinations at 20°C. Qualitatively the results were similar as those at 50°C, but the amount and the stability of the foam were less for powders from homogenized milk. The upper layer of the milk in this case consisted partly of undissolved powder particles i.e. scum.

Sample 1k appears to be a special case. Reconstituted milk from it showed only a small amount of scum. After one hour a thick layer of sediment was observed, consisting mainly of clustered fat globules and casein, originating from poorly dissolved powder particles. This latter conclusion is based on microscopical examination of the sediment.

Consequently the fat content in the top layer of the milk is much lower than the calculated value g_c, as can be seen in Table 3. The dry-solids content in the top layer turned out to be 2/3 of the calculated value.

From the above results the conclusion may be drawn that the foaming of milk is not promoted by the free-fat content of the powders, but by a large number of small fat globules in the milk which are trapped in the interface between liquid and air. For scum formation the presence of powder particles with a low speed of dissolution is more important than the free-fat content of the powder.

This last conclusion is in disagreement with the view of Litman et al. (33) and of King (36). Litman and Ashworth (34) showed that with increasing total fat content of milk powders, the free-fat content as well as the amount of scum on the reconstituted milk increased sharply at about 26% fat. The formation of a fat-protein complex as suggested by these authors was based on the observation that extensive scum development was found on milk from powder stored at about 30°C, whereas little scum was observed if the powders were stored at 7°C. For this reason, they related scum development to the initial

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free-fat content of the powder. In our opinion their argument is rather weak because they only observed a qualitative relationship between free-fat and scum.

The microscopical observations by King (35) that the scum contains numerous clusters and clumps consisting of fat and protein can be easily understood, because probably many fat globules are trapped in the liquid-air interface. However, his conclusion that this is due to 'unprotected' fat globules is not supported by experimental results.

According to Table 3 no churning occurred if the milk was prepared from powders manufactured from homogenized concentrated milk, thus often with a low free-fat content. If, however, powders from non homogenized milk with a much higher free-fat content were reconstituted, churned butterfat did appear on the milk surface.

It is well known (39) that churning is difficult with homogenized milk. Probably not only the fat globule size but also the surface conditions of the fat globules play an important role. Little is known about the changes that may take place in this respect during homogenization of the concentrated milk, as we pointed out in 4.3.3.

Compared with the amounts of free fat, the amounts of churned butterfat are small.

When considering the results in Table 3 a correlation is indeed found between free-fat content and churning of the butterfat, but possibly fat globule size and perhaps the clustering of fat globules in powders from non-homogenized milk influence both the free-fat content and the churning during reconstitution. Thus there is no strict evidence that there is a causal relationship between free fat and churning.

Conclusions: With the 20 powders investigated, varying widely in free-fat content, no correlation could be observed between cream rise and the amount of free fat in the powders. The same may be said of the foaming of the milk during reconstitution.

Churned butterfat was only observed on reconstituted milk from powders prepared from non-homogenized concentrated milk with high free-fat content, but the two quantities showed no quantitative correlation.

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5. Cohesion
Determination, influence of particle size, moisture content and free-fat content

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Abstract

The unconfined compression test, well known in soil mechanics, was applied to determine cohesion in spray-dried whole milk. A powder plug is formed with a certain consolidation pressure and placed on a topscale balance. A slowly increasing vertical force is exerted on the powder plug and the stress at failure can be read from the balance. From this quantity and the shearing angle, the cohesion can be calculated. The 95% confidence limit for a mean of 5 repeats was about 6%.

Cohesion thus found is influenced considerably by the consolidation pressure P. Most measurements were carried out with $P = 0.08$ kg/cm². Good agreement with visual observation of stickiness was found.

Cohesion of spray-dried whole milk increases with decreasing particle size as expected. Unexpected, however, was that the cohesion is independent of fat content in the range 20–45% fat and of free-fat content. In spite of this, experiments at different temperatures showed that the milk fat is an important factor in the cohesion, and it is suggested that only a small amount of surface fat on the particles is sufficient to give cohesion to whole milk powders. Probably fat contents higher than 20% result in more surface fat, but this does not increase the cohesion.

It is shown that an increase of moisture content decreases the cohesion in the range 2–4%, but a strong rise of cohesion occurs in the range 4–7%, probably due to increased plasticity of the powder particles and to lactose crystallization.

5.1 Introduction

A distinct disadvantage of whole milk powder in respect of storage in bulk, automatic conveying or packaging and reconstitution properties, is its stickiness. Attempts were undertaken to reduce the stickiness by adding free-flowing agents (1).

Usually the large difference in stickiness between dried skim milk and dried whole milk is attributed to the presence of fat in the latter, especially the free-fat (2).

Several investigations have been made in attempts to describe the rheological

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properties of dried milk in terms of free-flowability, internal friction or cohesion between the powder particles (1, 3, 4, 5, 6, 7). Most of the methods applied are suitable for free-flowing powders such as non-fat dry milk, agglomerated skimmed milk powders or sticky powders to which free-flowing agents had been added, but fail with normal whole milk powders. Often such powders are not free-flowing at all, because the cohesion between the particles overcomes the effect of gravity. Probably the internal friction is of minor importance in these cases.

Taneya (5) observed two types of flow, viz particle flow, where every particle moves as an independent unit, and bloc flow, where the particles are agglomerated into blocks owing to their cohesion. Dried whole milk showed small-block flow mixed with particle flow, whereas dried skim milk showed typical particle flow. This author measured the internal friction of dried milk (4) by a direct shear test, which principle was also applied by Hayashi et al. (7) to non-fat dry milk. Later on Taneya (5, 6) applied a double-cylinder type viscometer to determine both the internal friction and the cohesion of dried milk.

We modified a simple method, well known in soil mechanics, for the determination of the cohesion in sticky milk powders. The method and some of the results are described below. With this method the influence of particle size, moisture content, fat content and free-fat content on the cohesion of dried whole milk were studied.

It is common use in soil mechanics and powder technology to use the term cohesion or cohesiveness for the mutual attraction of powder particles of the same kind.

In spite of efforts devoted to its elucidation it is still difficult to describe it in terms of well defined physical or chemical parameters. The reason is the small size of the particles and the difficulty of assessing not only the forces acting between them, but also their geometrical arrangement, which is important.

Brown and Richards (8) use the following definition: 'Cohesion is the sticking of the components of a bulk solid to one another and is conveniently assessed as the resistance of a powder to shear at zero compressive normal load.'

For convenience we shall use this definition, although we applied a small normal load in our method.

Particle size, moisture content, fat content and free-fat content were determined as described earlier (9, 10).

5.2 Description of the method

Undoubtedly soil mechanics is the oldest field of science in which, for practical reasons, efforts were undertaken to determine quantitatively the mutual co-

hesion between fine particles. Three methods have been used to measure internal friction and cohesion of soil:

a. The direct shear test
b. The triaxial compression test
c. The unconfined compression test.

The latter is probably the oldest and simplest method intended for field work, but it can only be applied with cohesive soil which exhibits a low plastic deformation under pressure. Axial compression is applied to a cylindrical specimen of undisturbed soil and the stress at failure of the sample is determined (11, 12, 13). Similar experiments with dairy products have already been reported in 1937 by Davis (14). This author used cylindrical plugs of cheese and butter.

In principle the unconfined compression test can be used for milk powders if the stickiness is sufficient to enable one to form cylindrical powder plugs strong enough for further handling. We applied this method as follows: A powder plug of 40 mm diameter was formed in a perspex box with a cylindrical hole, which could easily be split into two halves.

Various consolidation pressures P can be exerted by a good fitting p.v.c. cylinder on top of the powder. The performance is shown in Fig. 1. Before
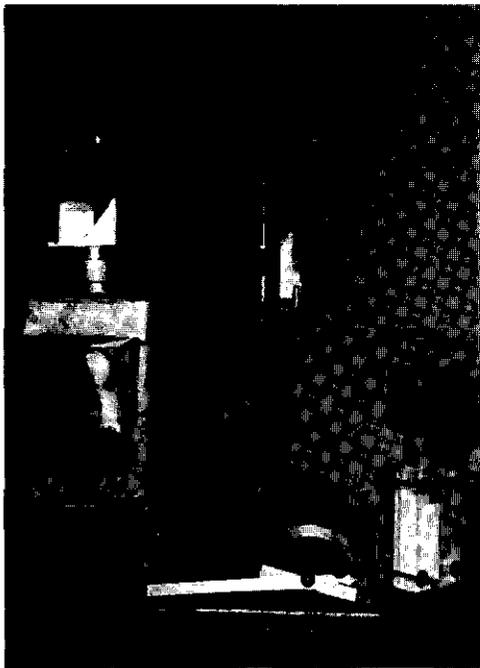
Fig. 1. Performance of the cohesion measurement by the unconfined compression test.

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filling the hole with powder a Perspex disc is inserted on the bottom to facilitate transportation of the powder plug. The wall of the hole was polished from time to time to prevent adhesion of the powder particles to it. Preliminary experiments showed that the way of filling the cylinder with powder, viz in one time or in portions with intermediate consolidation, did not influence the stress at failure. Consolidation time was standardized to 3 minutes. It made no difference whether this time was 30 seconds or 30 minutes.

The powder plug in the Perspex box is placed on the scale of a Mettler balance (maximum weight 2 kg), and dismantled on the scale. The balance scale is level and the end planes of the powder plug are exactly parallel. The powder cylinder is then inspected for fractures, and fractured plugs are discarded. An exactly horizontal plate is then placed on top of the powder plug and moved down slowly with a displacement of 1 mm per revolution. In this way an increasing axial force is exerted on the powder plug. The force at failure can be read from the balance with an accuracy of 1 g (Fig. 1).

From this result the cohesion C can be calculated according to the rules of soil mechanics (11, 12). This is illustrated in Fig. 2. The angle between the shear plane and the vertical α depends on the angle of internal friction φ as follows: $\alpha = 45 - \frac{1}{2}\varphi$.

With a simple goniometer α was estimated experimentally with an accuracy of $\pm 1°$. The cohesion C can be calculated from the following equation:

$$C = \frac{1}{2}p \cdot tg\,(45 - \frac{1}{2}\varphi) = \frac{1}{2}p \cdot tg\,\alpha. \tag{1}$$

p being the stress at failure; $p = F/A$, wherein $A = 1/4\,\pi \cdot D^2 = 12.5\ cm^2$. For the formation of a good shear plane the height of the cylinder should obviously exceed D. ctg α.

In this way the angle of internal friction φ as well as the cohesion C can be determined. Unfortunately the reproducibility is not very good. We therefore perform all measurements in quintuplicate and the average values are sufficiently accurate for practical purposes. A few results are shown in Table 1, to illustrate the reproducibility of F as well as of α.
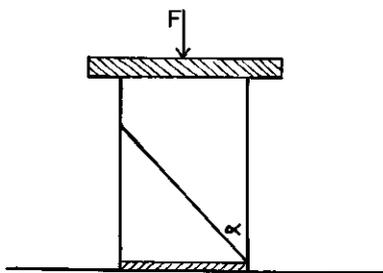

Fig. 2. Schematic diagram of powder plug under stress.

Table 1. Shear stress at failure F, shear angle α, powder density ϱ_p and cohesion C of spray-dried whole milk, determined with different consolidation pressure P.

Sample number	P (g/cm^2)	ϱ_p (g/cm^3)		F (in g) and α (in °) in quintuplicate					Av.	C = F/2A. tg α (g/cm^2)
A	0.08	0.60	F	170	200	190	160	180	180	5.2
A	0.08	0.60	α	36	36	36	37	35	36°	
A	0.16	0.62	F	215	210	210	245	225	220	6.4
A	0.16	0.62	α	35	35	38	35	38	36°	
A	0.40	0.68	F	295	305	320	305	300	305	8.5
A	0.40	0.68	α	36	36	35	34	32	35°	
B	0.08	0.60	F	195	185	195	210	210	200	5.8
B	0.08	0.60	α	35	34	36	39	35	36°	
B	0.16	0.62	F	285	280	290	270	250	275	7.7
B	0.16	0.62	α	38	36	36	34	33	35°	
B	0.40	0.65	F	390	385	400	415	405	400	11.6
B	0.40	0.65	α	38	35	36	37	35	36°	
C	0.16	0.61	F	200	260	250	260	280	250	6.2
C	0.16	0.61	α	32	32	33	32	32	32°	
C	0.40	0.64	F	320	420	420	390	390	390	9.8
C	0.40	0.64	α	32	31	33	32	33	32°	
C	0.80	0.65	F	420	430	460	410	400	425	10.6
C	0.80	0.65	α	31	32	32	32	32	32°	

The standard deviation of the mean of 5 repeat measurements was found to be about 3%, so that the 95% confidence limit was less than 6%.

From Table 1 it can be concluded that the cohesion is considerably influenced by the consolidation pressure P. This was to be expected because the density of the powder plug, and thus the number of contact points between the particles per unit volume, increases with P. For the same reason the cohesion of the small particle fractions is higher than that of the main fractions. Fig. 3 illustrates the above phenomena. We shall return to this subject when more data are available.

In dairy practice consolidation pressures upto 1000 g/cm^2 may occur, when powdered milk products are stored in silos. Usually, however, the pressures will be much lower, say about 100 g/cm^2 or below and they are more important for most purposes, e.g. storage in paper bags or packaging. Therefore further measurements were performed with consolidation forces of 1 or 2 kg, yielding pressures of 80 and 160 g/cm^2.

The shear angle α with spray dried whole milk usually varies from 30–36° with an average value of 32°. For routine measurements and in those cases where we were not able to estimate α with sufficient accuracy, we therefore
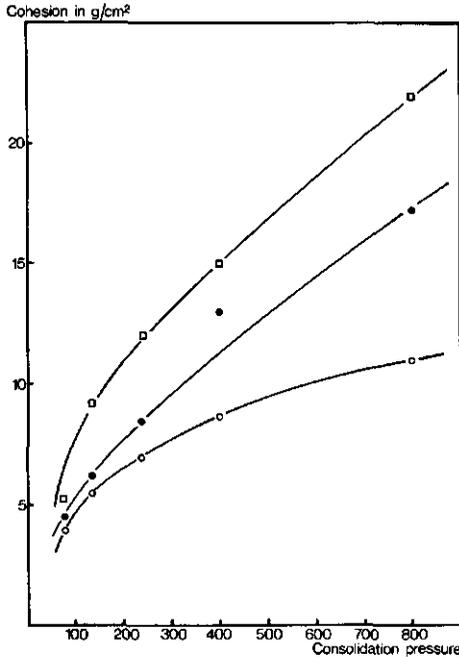
Fig. 3. Cohesion (g/cm²) of spray-dried whole milk in dependence of consolidation pressure (g/cm²) and mean particle size.
□ d̄ = 20 μm; ● d̄ = 27 μm; ○ d̄ = 40 μm.

applied the following equation:
$$C = F/40 \text{ g/cm}^2 \tag{2}$$
the cross sectional area A being 12.5 cm² and tg 32° being 0.62.

From the above it may be concluded that the angle of internal friction varies from 18° to 30°, with an average value of 26°. Coefficients of internal friction computed from these results, being 0.32–0.58 with an average value of 0.49, agree well with those obtained by Taneya and Sone (4), whereas several values obtained by Hayashi et al. (7) for non-fat dry milk lie in the same range.

5.3 Stickiness and cohesion

An important question was if there was a good correlation between the cohesion as determined above and the stickiness observed visually and tactually in dairy practice. This was checked by estimating the cohesion of 25 spray milk powders with fat contents of 20–40 % after applying a consolidation pressure of 0.08 g/cm², and comparing the results with those obtained by a test panel, consisting of 4 persons who judged stickiness visually and tactually.

In the latter case the test was carried out by judging the powders in two groups of 15 samples. The second group contained a few samples of the first

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group to check the repeatability of the judgement. The test panel was asked to qualify the stickiness of the powders with a mark between 0 and 10 in comparison with two standards, which were a free-flowing skim milk powder marked as 0 and a very sticky whole milk powder marked as 10. Stickiness of the powders was judged by observation of the behaviour of the powders during stirring the powder in 1-1b tins with a spoon. It turned out to be rather difficult to judge the stickiness of spray-dried whole milk visually. Large differences are easy to detect, but powders with a moderate free-flowingness are troublesome.

Average values of 25 powders obtained by the 4 persons were 8.4, 6.8, 5.9 and 7.7, respectively, the differences being mainly due to the results with a minor proportion of the powders. Corrections for systematic individual errors were not possible, because with some powders the 4 judges showed a high degree of agreement, whereas in other cases they differed widely in their judgement.

The results with powders included in both series of tests showed that the reproducibility was good, the difference being 0.5 point or less.

Nevertheless there is a strong correlation between the test results and the cohesion as shown in Fig. 4, where average stickiness S is plotted against C. The correlation coefficient appeared to be 0.85, yielding a residual standard deviation in S of 1.1. The equation of the regression line is:

$$S = 0.89\,C + 1.9. \tag{3}$$

A statistical analysis by the F-test showed that the residual spread is higher than may be ascribed to the differences between the judges. Thus the deviations
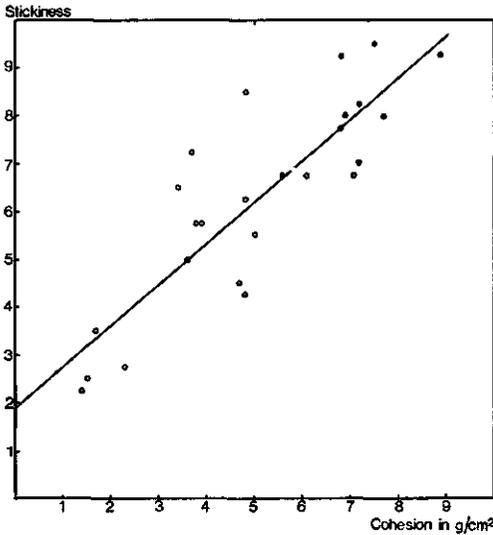

Fig. 4. Correlation between visual stickiness and cohesion. ○ main fractions; ● cyclone fractions.

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of the regression line are not due to the inaccuracy of the tests only, but there is a certain real difference between the visual test results and the cohesion determined as described in the preceding section. Evidently the stickiness of milk powders cannot be described completely by the cohesion alone.

Nevertheless, in the following only the cohesion will be considered, because it is an objective quantity and is also more accurately estimated than the visual stickiness.

The unconfined compression test was chosen because it can be carried out very conveniently with a minimum of simple apparatus yielding an approximate value for the stickiness of spray-dried whole milk.

5.4 Cohesion in relation to moisture content

It seems quite natural that the moisture content of a spray-dried milk product should influence the cohesion of its particles. Both lactose and protein may become more sticky when they have absorbed moisture. The plasticity of
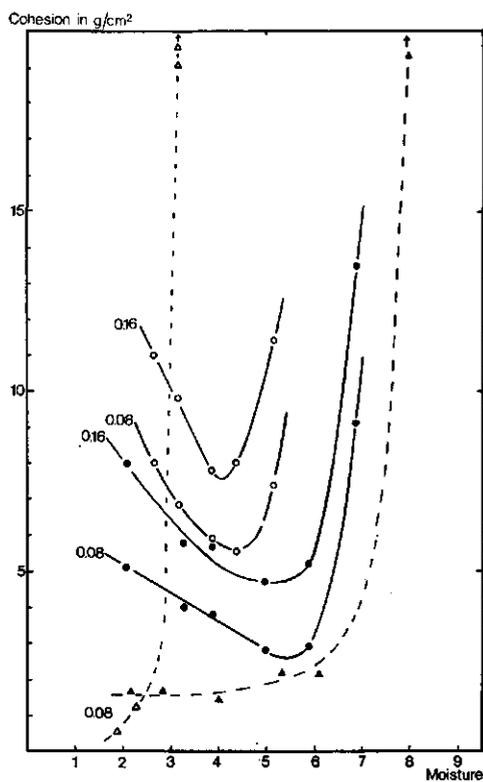
Fig. 5. The relationship between moisture content (%) and cohesion (g/cm²) of spray-dried whole milk (○ ●) and spray-dried whey (▲ △). Consolidation pressures 0.08 and 0.16 kg/cm².

the particles may vary with moisture content, changing the contact area between the particles under pressure.

The influence of moisture content on cohesion was studied with several spray-dried milk products by allowing the powders to absorb moisture from moist air and by estimating the cohesion at different moisture levels. Moisture content was determined by weighing a powder sample before and after drying for 2 hours in vacuo at 105°C.

Results obtained with two whole milk spray powders shown in Fig. 5, clearly demonstrate that their cohesion indeed is considerably influenced by the moisture content. Cohesion at first decreases when the moisture content is increased from 2% to about 4%, but at higher values the cohesion increases sharply. Other whole milk powders (4 samples) showed the same relationship. With several other spray-dried milk products (powdered baby food) we found similar curves. It would be interesting to know how non-fat dry milk behaves, but we were not able to form powder plugs of such powders.

It was possible, though, to carry out measurements with spray-dried whey but the results differed widely as is illustrated with 2 powders in Fig. 5. Considerable fluctuations occurred in the curves of two other whey powders, possibly due to an unequal distribution of moisture in them. Measurement of the shear angle was difficult if not impossible, but the stress at failure could be determined with a good reproducibility.

Nevertheless two conclusions are possible with the results obtained so far:
1. Cohesion in spray-dried whey is higher than in spray-dried skim milk with the same average particle size at a moisture content of 2–3%. Assuming that the composition of the surface is the same as that of the particle as a whole, it may be concluded that lactose is more sticky than casein;
2. Cohesion in spray-dried whey does not decrease materially with increasing moisture content in contrast with the behaviour of spray-dried whole milk. The latter can be explained by swelling of the casein with moisture absorption. Surface folds or cracks may disappear resulting in a lower 'apparent' cohesion.

We believe that the strong rise of cohesion both with spray-dried whole milk and spray-dried whey is due to increasing stickiness of the lactose glass and lactose crystallization. The latter was observed under the polarizing microscope in a few cases at high cohesion values. Lactose crystals on the particle surface as observed by Taneya (15) and clusters of powder particles kept together by crystalline lactose bridges may contribute to a high apparent cohesion. Moreover increased plasticity of the particles at moisture contents of 5–7% may have contributed to a higher cohesion.

When studying the influence of free-fat or fat content on the cohesion of spray-dried whole milk, the moisture content must be taken into account.

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5.5 Influence of fat content, free-fat content and particle size on cohesion

A series of powders with fat contents ranging from 10 to 60%, part of which were applied in earlier investigations (10,16), was used. The preparation was described in a preceding report (10).

All powders with the same fat content were prepared from one batch of concentrated milk. Main and cyclone fractions of a powder are marked with a and b, respectively, and powders from that part of the batch which was homogenized prior to spray drying are marked with H.

Cohesion was determined as described in Section 5.2. It was not possible to form plugs from powders with 10% fat with a consolidation pressure of 0.08 kg/cm², because the powders were rather free-flowing. Powders with 50% fat, or more, often adhered to the wall of the Perspex box and fractures were caused by the dismantling of the plugs. Because of the unreliable results we discarded such powders.

Normally the mean particle diameter of the main fractions of our powders is twice that of the corresponding cyclone fractions as shown earlier (10, 17). Mean particle size is characterized by the specific surface area as determined by permeatry.

The moisture content ranged from 1.0–2.5% and free fat was determined by two methods as described in a preceding paper (9).

From the results shown in Table 2 the following conclusions can be drawn;
1. Cohesion is higher in the fine particle cyclone fractions than in the corresponding main fractions;
2. Within the groups of powders with approximately the same particle size, the cohesion is independent of the fat content in the range 20–45% fat;
3. There is no correlation between the free-fat content and cohesion of powders with approximately the same particle size, even if the free fat is expressed per unit surface area. This is illustrated with Fig. 6 in which the cohesion is plotted against free-fat content as determined by the short extraction method.

Conclusion 1 was expected because it is well known in powder technology that fine powders are more cohesive than coarse powders of the same kind.

Conclusion 2 is somewhat unexpected because it is well known in dairy practice that skim milk powders are much less cohesive than whole milk powders. Moreover spray-dried whole milk is rather free-flowing at about 4°C whereas the same powder is sticky at 40°C. A similar observation was reported by Tripp et al. (18). This is illustrated by a few powders in Table 3. Cohesion was determined at the temperatures mentioned in the table and the powders were stored at least 24 hours at these temperatures before the measurements.

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Table 2. Cohesion of spray-dried milk with varying fat content, free-fat content and particle size.

Sample No	Fat content (%)	Moisture content (%)	Specific surface area (cm²/cm³)	Free fat		Cohesion (g/cm²)
				10 min, 22°C	7 h, 44°C	
8a	20.1	2.1		2.7	3.5	3.8
8b	20.0	2.1		14.7	19.0	4.8
9a H	20.3	1.7		1.3	1.4	2.3
9b H	20.2	1.2		3.9	3.9	4.5
C10a	20.1	2.6		2.1	3.0	4.8
C10b	20.1	2.3		25	32	7.5
11a	25.7	1.9	1440	3.1	13.0	6.1
11b	25.7	1.8	2730	34	44	7.6
12a H	25.7	1.7	1430	1.5	1.5	7.1
12b H	25.7	1.5	2520	7.1	7.4	8.9
13a	30.3	1.2	1240	8.7	47	1.7
13b	30.0	1.7	2500	61	74	6.8
14a H	29.7	2.7	1170	1.1	1.3	4.8
14b H	29.8	2.0	2360	6.1	6.7	6.9
C15a	29.9	2.0	1130	10.4	33	3.9
C15b	29.8	1.7	2880	79	79	6.8
C16a H	30.1	1.5	1000	1.0	1.1	5.0
C16b H	30.1	1.7	2000	6.6	6.7	7.2
17a	35.5	1.8	1150	8.4	59	1.5
17b	35.2	2.2	2390	73	84	7.7
18a H	34.9	3.3	1020	1.9	1.9	4.7
18b H	35.2	2.7	2180	10.0	12.2	5.6
19a	40.3	1.1		10.3	63	3.6
19b	40.0	1.3		74	84	8.0
20a H	40.1	1.6		1.5	2.6	5.0
20b H	40.2	1.5		16.6	21	5.3
C21a	40.1	1.5		7.3	46	5.4
C21b	39.8	1.3		77	86	6.4
C22a H	40.2	1.4		1.2	1.5	5.1
C22b H	40.2	1.2		17.8	20	5.7
23a	45.5	1.1		13.5	73	3.4
23b	45.1	1.3		77	87	8.6
24a	45.1	1.5		3.4	28	5.1
24b	45.0	2.1		27	45	7.4

The figures in Table 3 show that the cohesion at 4°C is much lower than at 20°C. Except with sample 11b the difference in cohesion at 20°C and 40°C is not significant.
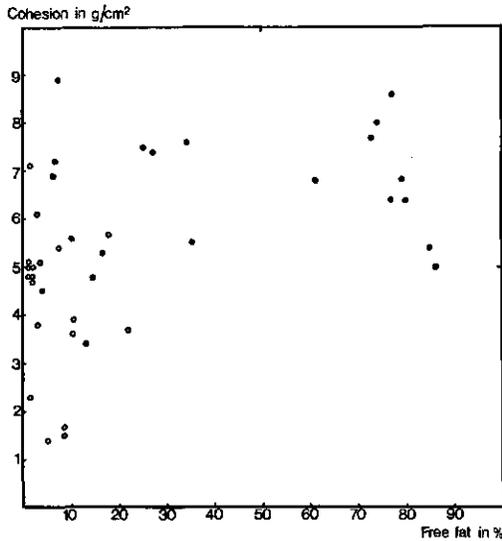
Fig. 6. The relationship between cohesion and free-fat content of spray-dried whole milk. ○ main fractions; ● cyclone fractions.

A few other experiments were performed with four whole milk spray powders of which powder plugs were formed at 20°C with a consolidation pressure of 0.8 kg/cm². In this case a much higher consolidation pressure was chosen to have powder plugs more suitable for further handling. These plugs were stored in closed tins at 5°, 20° and 40°C for 7 days. After that time the cohesion in the powder plugs was determined as usual but half the plugs were stored at 20°C for several hours prior to the measurement. The results shown in Table 4 clearly demonstrate that the cohesion in the powder plugs is much increased by the storage at 5°C. The effect is reversible, for if the plugs are warmed up from 5°C to 20°C prior to the measurements, the cohesion therein is almost equal to that found at 20°C without further treatment of the plugs.

Without doubt the crystallization of the milk fat is the cause of the above

Table 3. Cohesion in spray-dried whole milk at 4°, 20° and 40°C.
Consolidation pressure 0.08 kg/cm².

Sample No	Cohesion (in g/cm²)		
	4°C	20°C	40°C
11a	2.3	6.1	5.7
11b	4.3	7.6	10.3
12a H	2.3	7.1	6.6
12b H	2.4	8.9	9.1

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Table 4. Cohesion in whole milk powderplugs formed at 20°C and stored at 5, 20 and 40°C. T_m = measuring temperature. Consolidation pressure 0.80 kg/cm².

Sample No	Free fat 10 min, 22°	Cohesion in g/cm²				
		7 days at 5°C		7 days 20°C	7 days at 40°C	
		$T_m = 5$°C	$T_m = 20$°C	$T_m = 20$°C	$T_m = 20$°C	$T_m = 40$°C
29a	1.9	43	11.6	13.3	16.6	14.9
29b	9.1	>50	25	30	40	36
30a	1.2	41	10.3	14.2	13.2	13.1
30b	2.9	>50	29	34	29	43

phenomena. At 40°C the butterfat is completely liquid, and at 20°C for the major part, whereas at 5°C most of the butterfat is solid. If the particles are brought into contact after the fat has solidified, the subsequent cohesion is much lower than at 20 or 40°C, but if they are in contact when the fat is liquid, the solidification causes the formation of crystalline fat bridges between the particles, which greatly increase the cohesion in the powder plugs. But only the surface fat on the powder particles and not total free fat contributes to this effect.

With a scanning electron microscope we often observed bridges between particles of spray-dried whole milk which were probably fat bridges. An example is given in Fig. 7. We selected a photograph on which many surface folds in the particles can also be seen.

Conclusion 3 is in direct contradiction to that of Eisses (1). This worker found a correlation between free-fat content and free-flowingness of spray-dried whole milk, but disregarded the particle size. The latter may be the cause of the discrepancy.

When considering the above results, the following conclusions are possible:
a. The amount of surface fat of spray-dried whole milk increases with fat content until a fat content of about 20 % is reached, and the cohesion increases with the amount of surface fat. At higher fat contents the amount of surface fat remains constant with increasing fat content and so does the cohesion;
b. The amount of surface fat increases with fat content as reported by Pyne (19), but the cohesion between the powder particles is not further increased if a certain amount of surface fat per unit surface area is exceeded. This limit is reached already at a fat content of about 20 %.

In our opinion Conclusion b is more acceptable than Conclusion a because a small amount of surface fat is probably already sufficient to give cohesive milk powders.
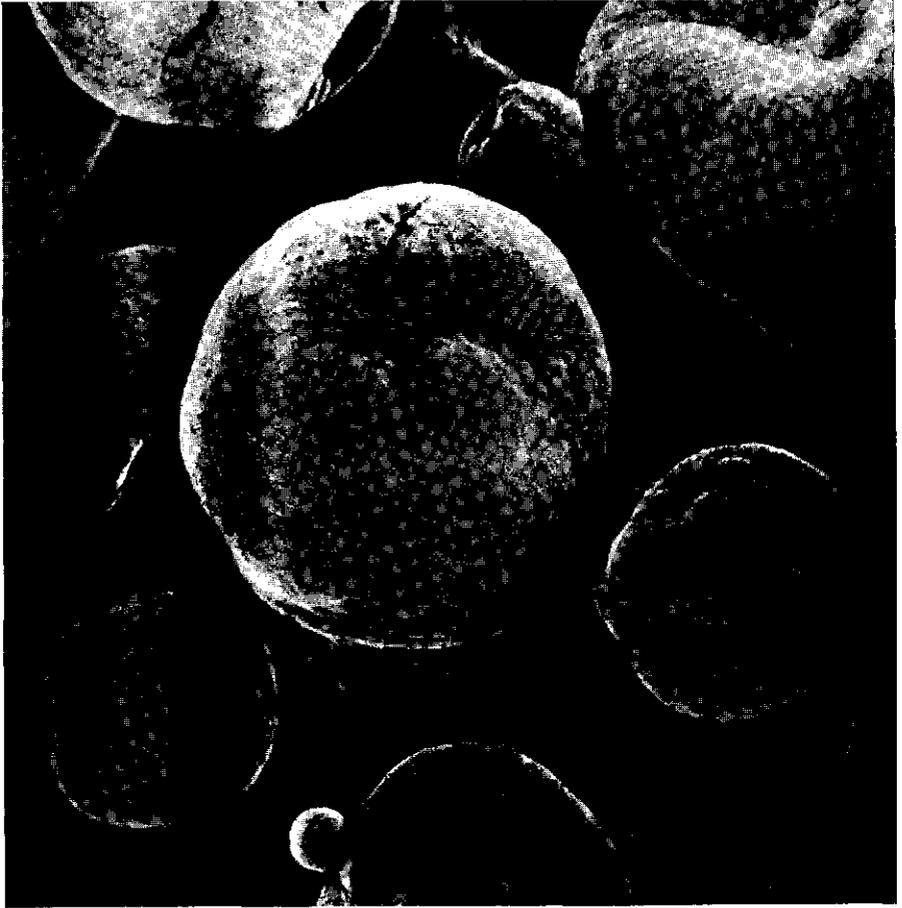
Fig. 7. Fat bridge between two particles of spray-dried whole milk and folds in the particle surface. Magnification × 1180.

As yet it is not exactly known which part of the free fat is surface fat. Earlier (20) we suggested that the surface fat can be determined by a short extraction at room temperature. In a subsequent report we shall return to this subject.

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6. A correlation between free-fat content and moisture content of whole milk spray powders

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Abstract

From the results of previous work we concluded that the micropores in whole milk powder particles might be related to the free fat content of these powders. Assuming that the pores arise in the last phase of the drying process, it seemed possible that the pores would reclose when the powder particles absorb moisture, resulting in a lower free fat content.

In agreement with this reasoning we found that when the moisture content of whole milk powders is increased in the range of 2–8 % the free fat content decreases considerably. At a critical moisture content the fat becomes extractable quantitatively due to lactose crystallization.

Special features of the curves suggest however, that the process is more complicated than is assumed above.

6.1. Introduction

From the results of previous work we concluded that:
1. Small particles in whole milk powders contain much more extractable fat than do the larger ones (2).
2. The micropores in milk powders, first found by Berlin and Pallansch (1), are much wider or more numerous in the small particles of whole milk powders then in the larger ones (3).
3. It was natural therefore to suppose that the pore size in the particles might be related to the free fat content of whole milk powders (3). Indeed, it seemed possible that the fat globules inside the powder particles could be reached by fat solvents through the pores, if they were wide enough.

Assuming that the pores or cracks arise in the last phase of the drying process due to shrinkage of the material or to water vapour escaping from the interior of the particles, it seemed possible that the pores would reclose when the powder particles were allowed to absorb moisture. In view of Item 3 above, this should

result in a decrease of the free fat content with increasing moisture content of the whole milk powder, at least below the critical moisture content at which lactose crystallization starts. It is well known that in the latter case the fat becomes extractable quantitatively (4).

It therefore seemed worth while to determine the free-fat content in whole milk powders in relation to the moisture content. The results are described below.

6.2. Materials and methods

Any effect of a moisture increase on the free fat content of whole milk powders could hardly be expected if the initial free fat content were low. We therefore selected a number of powders with relatively high free-fat contents at a moisture level of 2–3 %. These were the cyclone fractions of powders used in earlier work (2).

The powders were pressure spray-dried and contained about 28 % of fat.

The procedure used in the measurements was as follows. Samples of milk powders were allowed to absorb moisture in the same way as described in a previous paper (3). The initial moisture content was determined by the Karl Fischer method, whereas the moisture increase was estimated by weighing. Free-fat contents of the powder samples at different moisture levels were determined in two ways as described earlier (2). The rapid method was to stir 5 g powder for 10 minutes with carbon tetrachloride at room temperature. After filtration the dissolved fat was estimated by weighing the residue after evaporation of the solvent. The second, more time consuming method, was to extract 5 g of powder with petroleum ether for 7 hours in a Soxhlet apparatus. After filtration and evaporation of the solvent, the residue was weighed. This method almost always yields a considerably higher free-fat content than the first method.

All moisture and free fat determinations were carried out at least in duplicate. Free-fat contents are expressed as a percentage of the dry solids.

At each moisture content, powder samples were examined between crossed nicols under the microscope, in order to determine the point at which visible lactose crystallization started.

6.3. Results and discussion

Experiments were carried out with four different powders and the results are shown in Fig. 1 and 2, where we have plotted the free-fat content of the powders against the moisture content. Both figures show that when the moisture content is increased the free-fat content of whole milk powders decreases considerably.

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free_fat content in %

● MM
● TA
x ML
▲ VA

moisture content in %
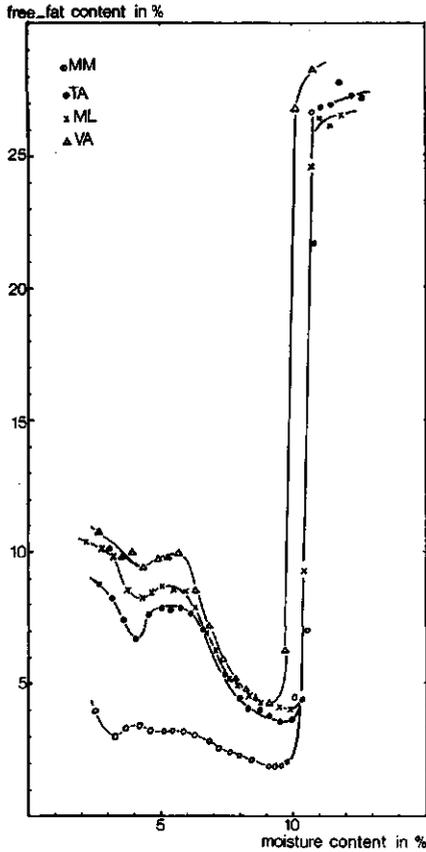
Fig. 1. Free-fat content of whole milk powders, determined by the rapid extraction method, in dependence of the moisture content.

When the short extraction method is used a sudden rise of the free fat content is observed at a moisture content of 9–10% (Fig. 1). At higher moisture levels the fat can be extracted quantitatively. Microscopical examinations proved that at that point all powder particles contain lactose in the crystalline state. In a few particles traces of crystalline lactose were already observed at a moisture content of 7%.

Evidently the crystallization starts at that moisture level but the number or the size of the inter-crystalline cracks is too small for the dissolution of the fat to be attained in the 10 minutes available. This can be concluded from Fig. 2, in which it is shown that when the extraction is extended to 7 hours at a temperature of 45–50°C (i.e. the second method), the free-fat content already begins to rise at a moisture level of 6–7%.

The critical moisture level at which the lactose crystallizes and the fat in

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free_fat content in %

- MM
- TE
x ML
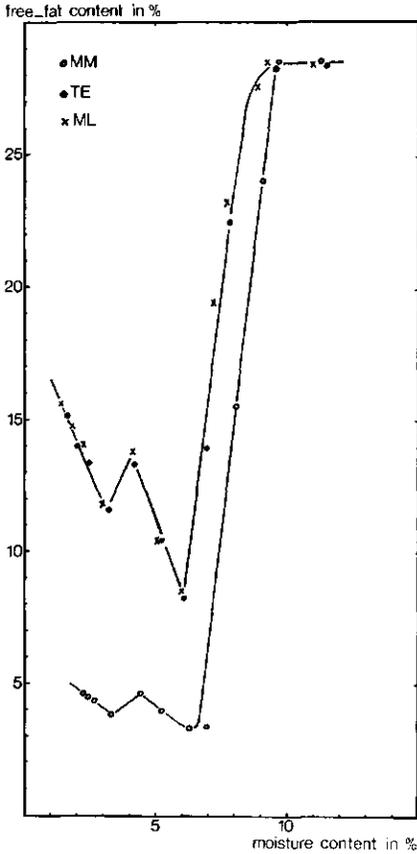
Fig. 2. Free-fat content of whole milk powders, determined by 7 hours extraction with petroleum-ether, in dependence of the moisture content.

moisture content in %

whole milk powders can be extracted quantitatively, was first found by Lampitt and Bushill in 1931 (4). They showed that this effect is irreversible; indeed when, after lactose crystallization the powder was redried, the free-fat content remained constant. In the moisture range below the critical level they also carried out a number of measurements, but with powders containing relatively little free fat, and concluded that the free fat content is constant in this range. In view of our results we examined their data more closely and found (Table 6) a slight decrease of the free fat content when the moisture content was raised from 2 to 7%, which confirms our results.

The changes taking place in the powder particles due to moisture absorption, resulting in a lower free fat content at higher moisture levels, proved to be reversible, as long as the critical moisture level was not exceeded. We found that when a whole milk powder is allowed to absorb moisture to about 8% and is then redried to the original moisture content, the free fat content as estimated

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Table 1. Free fat content (rapid method) of whole milk powders at the original moisture content (I), after moisture absorbtion (II) and after redrying to the original moisture content (III).

Sample number	I moisture %	I free fat %	II moisture %	II free fat %	III moisture %	III free fat %
1	3.6	8.9	8.4	4.5	3.6	8.8
2	3.9	8.4	8.2	4.8	3.9	9.9
3	4.7	8.5	8.3	4.7	4.7	7.4
4	6.3	8.0	8.4	4.5	6.3	7.3
5	3.3	9.9	6.2	8.1	3.3	10.3
6	4.2	3.4	7.4	2.5	4.2	2.8

by the rapid method returned to approximately its initial value. This is illustrated with a few figures in Table 1.

The 'irregularities' in the curves of both Fig. 1 and 2 around 4% moisture are without doubt significant. We have as yet no explanation for this behaviour.

A comparison between Fig. 1 and Fig. 2 shows that the free fat content in this moisture range is considerably higher when the time of contact is extended and the temperature is raised.

In view of the theory mentioned above it is interesting to note that Radema (5) found that the tallowy flavour of milk powder which develops during storage is reduced when the moisture content of these powders is increased. It is possible that the oxygen reaches the fat globules inside the powder particles preferably by way of the pores in the particles.

The phenomena mentioned above support the theory that the free fat in whole milk powders without crystalline lactose consists, at least partly, of fat inside the powder particles, which is extracted by fat solvents penetrating through pores or cracks. It is assumed that the pores arise in the last phase of the drying process. However, in view of the 'irregularities' in the shape of the curves in Fig. 1 and 2, the phenomenon is probably more complicated than that. In a following paper we hope to return to this subject.

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7. Particle structure of spray-dried milk products as observed by a scanning electron microscope

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7.1 Introduction

The internal structure of spray-dried milk particles has been studied by electron microscopy by several workers (1, 2, 3). However, in the preparation methods which have been applied until now, water was used, which may have caused considerable changes in the physical structure of the particles.

The first attempts to study the particle surface of spray-dried skim milk were undertaken by Taneya (4), who used a replica technique. At a conference at Ayr, Prentice (5) recently showed photographs of dried milk particles taken with a scanning electron microscope without water being used.

We applied a similar technique. Methods and a few results are given below.

7.2 Materials and methods

The powders were prepared with a Rogers-type pilot plant drier under the following conditions: dry-solids content of the concentrated milk or whey 40 %; spray pressure 80-100 kg/cm^2; nozzle 66/21; outlet temperature 80–90°C; Moisture content of the powders ranged from 1–2 %.

The samples were prepared for the electron microscope in a simple way. The particles were attached to the specimen holder by glue from 'sellotape', which had been dissolved in chloroform. One drop of this solution was transferred to the specimen holder and when, after some minutes, the chloroform had evaporated, some powder was sprinkled over the residual layer of glue. The excess particles were removed by a gentle spray of air. Finally the specimen was coated with carbon and gold in a vacuum evaporator. The scanning micrographs were made with a JEOL JSM-U3 scanning electron microscope at an accelerating voltage of 5–15 kV.

Considerable care must be taken to avoid artefacts with this technique. During observation under the microscope the energy dissipation in the specimen may cause cracks in the metal-carbon layer and in the particles. In particular, prolonged observation at a high magnification may be harmful. We therefore preferred to use a low magnification and kept the observation time as short as possible.

To reveal the internal structure of the particles it was necessary to break them. This was done by chopping up a small sample on a microscope slide with a razor blade. Although the efficiency of this method is very low, we obtained a sufficient number of broken particles. Whole milk powder particles with a relatively large central vacuole often have a rough cleavage surface, probably because they crack easily. The cleavage surface of particles of spray-dried skim milk or whey on the other hand is rather smooth, indicating that is was caused by cutting.

7.3 Results and discussion

Fig. 1 and 2 show the surface structure and the internal structure, respectively, of a few particles of the same whole milk powder. Small surface folds, cracks and
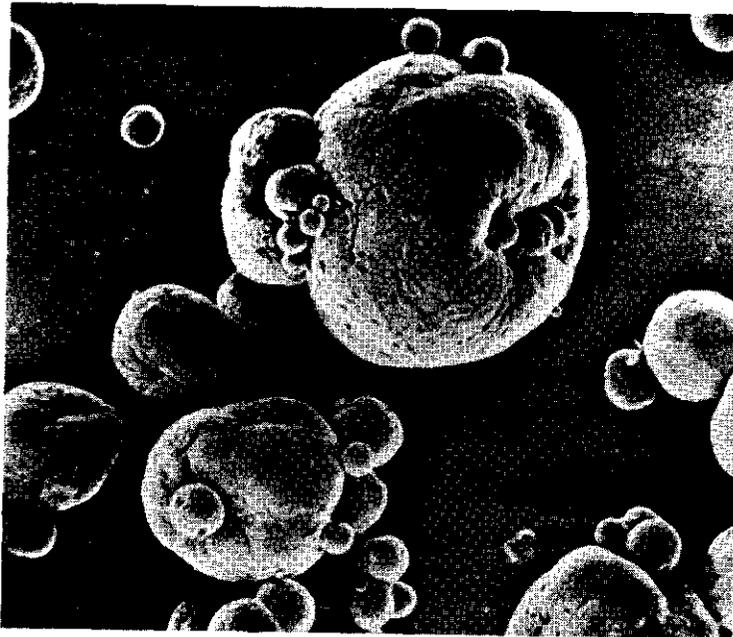

Fig. 1. Particles of spray-dried whole milk. Magnification × 950.
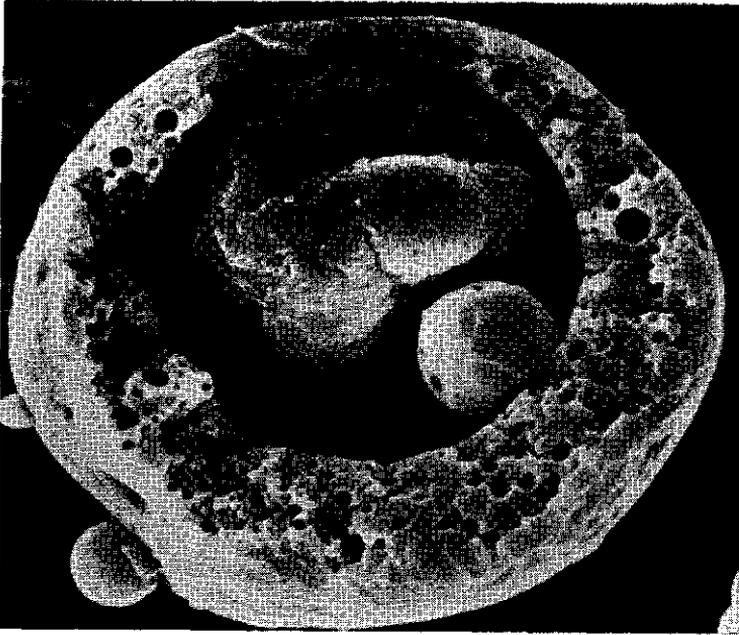
Fig. 2. Broken particle of spray-dried whole milk with large vacuole and trapped other powder particles. Magnification × 1925.
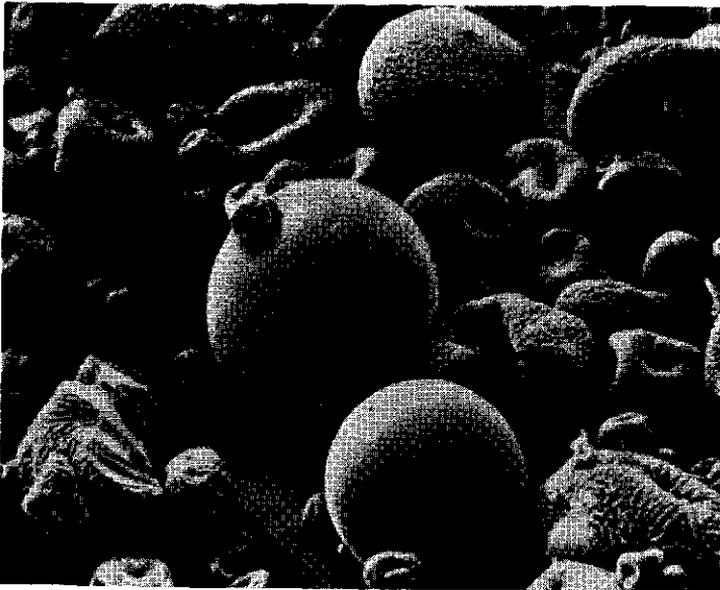

Fig. 3. Particles of spray-dried skim milk. Magnification × 290.
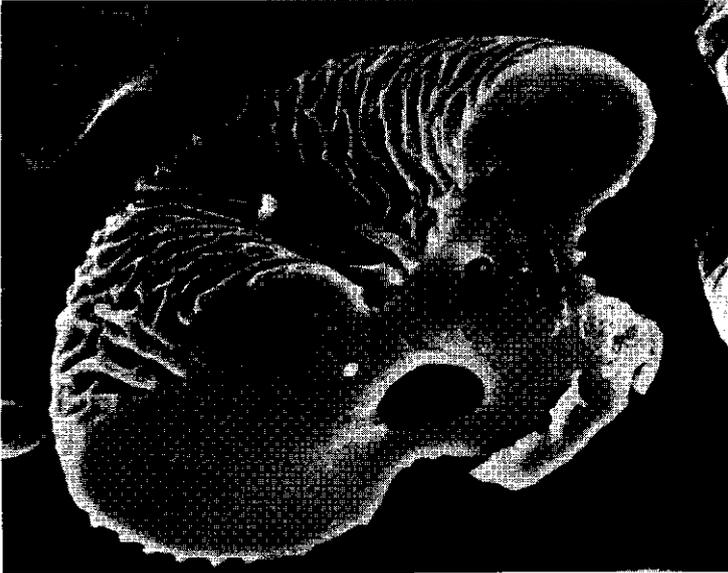
Fig. 4. Broken particle of spray dried skim milk with deep surface folds and a few small vacuoles. Magnification × 950.

a large vacuole with a few small powder particles trapped in it can be seen. Probably most of the holes in the cleavage surface had been occupied by fat globules, for such holes are not present in the cleavage surface of skim milk and whey powder particles (Fig. 4 and 6). Moreover the holes are smaller in broken particles of whole milk powders prepared from homogenized concentrated milk.

Particles of other spray-dried milks may show a different surface structure. Sometimes we found a very smooth surface, but we also observed particles with deep surface folds, resembling a cauliflower. Many samples contained particles with an 'apple-like structure' (Fig. 1). This is probably caused by an implosion during the last stage of the drying process or during the cooling of particles which contain a relatively large vacuole.

Fig. 3 shows that even in the same powder sample (skim milk) particles can have a very different surface structure. Particles with deep surface folds and with a smooth surface are both present, probably due to very different drying conditions of the individual particles. The difference in appearance of the particle surface of spray-dried whey (Fig. 5) and spray-dried skim milk (Fig. 3 and 4) suggests that the formation of deep surface folds is caused largely by the casein. Fig. 6 shows a whey powder particle with a large vauole.

More photographs will be published in subsequent reports.

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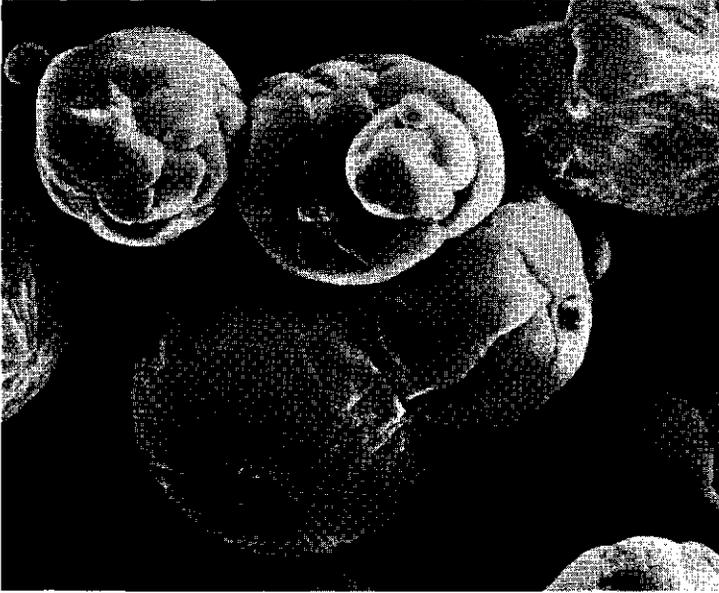
Fig. 5. Particles of spray-dried whey. Magnification × 950.
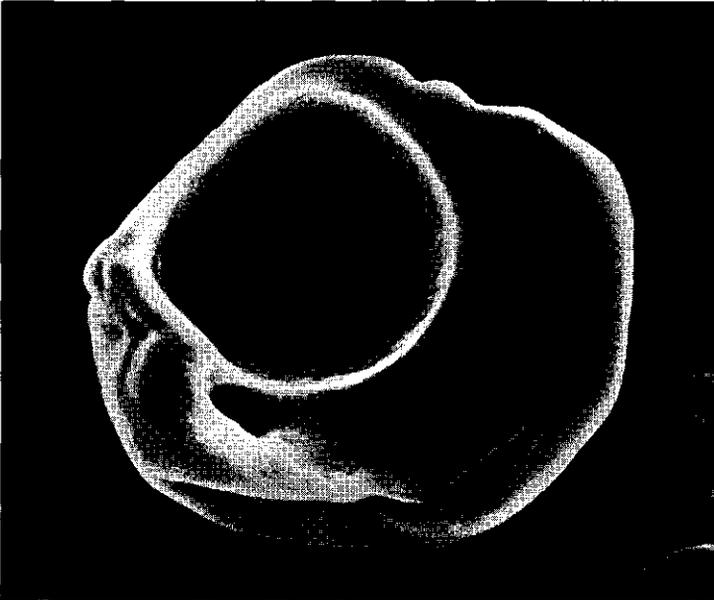
Fig. 6. Broken particle of spray-dried whey with a large and a small vacuole. Magnification × 1450.

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8. The relationship between free-fat content and particle porosity of spray-dried whole milk

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Abstract

From previous work we concluded that the pores or cracks present in whole milk powder particles might be related to the free-fat content of such powders. In the present report it is shown that there is a strong correlation (r = 0.94) between the free-fat content and the particle porosity of whole milk powders. From this observation it is concluded that the particle porosity is of major importance for the extraction of milk fat from whole milk powders. Other factors which may influence the free-fat content are the amount of surface fat on the particles and the spatial arrangement of the fat globules in the particles.

Photographs taken with a scanning electron microscope show cracks and pores in particles with high porosity, whereas in less porous powder particles only surface folds and occasional cracks could be observed.

Broken or cut particles show the vacuoles in the particles, but no capillaries connecting the vacuoles with the particle exterior. Possible explanations of particle porosity are discussed.

8.1 Introduction

During previous investigations we observed that:

1. Small particles of whole milk powders contain much more free fat than do the larger ones of the same powder even if the specific surface area is taken into account (1);

2. The penetration rate of air into particles of spray-dried whole milk is much higher for small particles than for the larger ones (2);

3. If the moisture content of spray-dried whole milk is increased in the range of 2–8 %, the free-fat content decreases considerably. The effect appeared to be reversible (3).

These facts can be explained in a natural way if the fat globules inside the powder particles can be reached by the penetration of fat solvents into the pores and cracks. The free-fat content would then depend on the porosity of the powder particles. Probably the pores or cracks arise in the last phase of the

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drying process due to uneven shrinkage of the material. We assumed that water absorption by the powder particles resulted in a reclosure of the pores or cracks to a greater or lesser extent, causing a decrease in free-fat content. Cracking due to temperature fluctuations during drying or cooling is possible, but seems less likely because the particle porosity of spray dried skim milk and spray-dried whey is very small (2).

The purpose of the present investigation was to find out if there is indeed a correlation between particle porosity and the free fat content of spray-dried whole milk. Results obtained with a considerable number of powders are shown below.

8.2 The penetration of gases into spray powder particles

Particles of spray powders usually contain vacuoles; these are filled with air at atmospheric pressure if the powders have been stored for some time under atmospheric conditions (1).

If such powder particles are exposed to gas with a higher pressure, the penetration rate of the gas into the vacuoles can be determined by means of a Beckman air pycnometer. This technique, in which the pressure p of the gas surrounding the particles is kept constant, was described earlier (2).

The penetration in relation to time can be calculated, if we assume that the gas flow through the capillaries into the vacuoles is governed by Poiseuille's law.

The volume flow rate dV/dt of a gas with a pressure p flowing through a capillary with a radius r into a volume B with pressure p_B is according to this law:

$$\frac{dV}{dt} = \frac{\pi\, r^4}{8\,\eta\, l} \cdot \frac{p^2 - p_B{}^2}{2\,p} \tag{1}$$

η being the viscosity of the gas and l the length of the capillary.

If the vacuole B is connected with the interparticle space by more capillaries (Fig. 1), Eq. 1 can be replaced by:

$$\frac{dV}{dt} = \frac{\gamma}{\eta} \cdot \frac{p^2 - p_B{}^2}{2\,p} \tag{2}$$

γ being a particle porosity factor of the form

$$\gamma = \sum_{r,l} \frac{\pi r^4}{8\,l} \tag{3}$$

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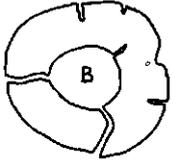
Fig. 1. Model of a spray powder particle with vacuole B and pores.

A volume of gas V of pressure p penetrating the vacuole results in a pressure rise Δp in B. Assuming that the gas flow in the capillaries is isothermal, we have:

$$\Delta p = \frac{V}{B} \cdot p \tag{4}$$

The pressure in B increases with time and is

$$p_0 + \frac{V}{B} \cdot p \tag{5}$$

p_0 being the pressure in B at the start of the experiment i.e. at $t = 0$. Thus at any time t the penetration rate of the surrounding gas into the vacuole can be described by inserting Eq. 5 in Eq. 2:

$$\frac{dV}{dt} = \frac{\gamma}{\eta} \cdot \frac{p^2 - [p_0 + (V/B) \cdot p]^2}{2} \tag{6}$$

or

$$\frac{dV}{dt} = \frac{\gamma}{\eta} \left\{ \frac{p^2 - p_0^2}{2p} - p_0 \cdot \frac{V}{B} - \frac{p}{2} \cdot \frac{V^2}{B^2} \right\} \tag{7}$$

Substituting $\dfrac{\gamma p}{\eta B} = a$ and $\dfrac{p_0}{p} = b$ \hfill (8)

yields the following differential equation:

$$\frac{dV}{A + CV + DV^2} = a.dt \tag{9}$$

in which: $A = \dfrac{B}{2}(1 - b^2)$; $C = -b$ and $D = -\dfrac{1}{2B}$.

The solution of Eq. 9 is:

$$\frac{1}{\sqrt{-q}} \cdot \ln \frac{2\,DV + C - \sqrt{-q}}{2\,DV + C + \sqrt{-q}} = at + K \tag{10a}$$

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in which $q = 4\,AD - C^2$. (10b)

Eliminating A, C, D and b from Eq. 10a and 10b yields

$$\sqrt{-q} = \left\{ \frac{p_0^2}{p^2} - 4\,\frac{B}{2}\left(1 - \frac{p_0^2}{p^2}\right) - \frac{1}{2B} \right\}^{\frac{1}{2}} = 1 \tag{11}$$

and

$$\frac{\dfrac{V}{B} + \dfrac{p_0}{p} + 1}{\dfrac{V}{B} + \dfrac{p_0}{p} - 1} = k e^{at} \tag{12}$$

Since for $t = 0$, $V = 0$, we find $k = \dfrac{p_0/p + 1}{p_0/p - 1}$ (13)

and:
$$\frac{\dfrac{V}{B} + \dfrac{p_0}{p} + 1}{\dfrac{V}{B} + \dfrac{p_0}{p} - 1} = \frac{\dfrac{p_0}{p} + 1}{\dfrac{p_0}{p} - 1} \cdot e^{at} \tag{14}$$

In all our experiments $p_0/p = 1/2$ (15)
namely $p_0 = 1$ kg/cm² and $p = 2$ kg/cm².

Substituting Eq. 15 in Eq. 14 gives:

$$\frac{1}{3} \cdot \frac{\dfrac{2V}{B} + 3}{1 - \dfrac{2V}{B}} = e^{at} \tag{16}$$

Eq. 16 is derived for one powder particle and can only be verified experimentally by estimating 2V/B as a function of time, if all particles in a powder sample have the same combination of γ and B. It is not impossible that these two factors indeed occur in certain combinations because particle porosity as well

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as the vacuoles may be caused by the same mechanism, viz the uneven shrinking of the powder material during drying.

In the next section a few experimental results will be shown with the purpose of checking the theoretical calculations.

8.3 Experimental check of the theoretical calculations

We carried out some measurements with a Beckman pycnometer to check Eq. 16. The sample cup containing 20.0 g spray-dried whole milk is connected to the measuring system of the pycnometer. To remove the air in this system it is evacuated rapidly and nitrogen is admitted.

After equilibrating for 5 min with nitrogen at atmospheric pressure, the measuring piston is moved inward during 30 sec until the gas pressure is 2.0 atm. As soon as this pressure is reached a stopwatch is started ($t = 0$) and the sample volume V_0 is read from the counter. This sample volume yields the mean particle density D_p, from which the vacuole volume B of the sample can be calculated. If the true density of the powder material D_t is known, we find:

$$B = V_0 (1 - D_p/D_t) \tag{17}$$

As described earlier (1), D_t can be determined by centrifuging suspensions of the powder samples in liquids with varying densities. When the sediment volumes are plotted against liquid density the intersection of the curve thus obtained with the density axis yields the true density, as the densest particles do not usually contain vacuoles.

The particle volume V_t is read from the counter of the pycnometer when the differential manometer is in zero position, indicating that the gas pressure in the measuring cylinder is equal to that in the reference cylinder. To keep the differential manometer in zero position, the measuring piston has to be moved inward continuously with time with some powders. The apparent sample volume is read from the counter at stated time intervals and the volume decrease yields the volume of gas with a pressure of 2 kg/cm^2 which has penetrated or has been absorbed in the powder particles in a given time.

In contrast with previous measurements (2) we used nitrogen as a displacement gas instead of air. This is because after 60 min with air we sometimes found a particle density exceeding the true density.

With nitrogen the particle density approaches the true density in such cases. Fig. 2 illustrates this observation. Evidently oxygen from the air is adsorbed or dissolved causing a too high apparent particle density. A few measurements with 2.0 g pure liquid water-free butterfat in the sample cup of the pycnometer showed that the absorption rate of oxygen in milk fat is about 50 % higher than
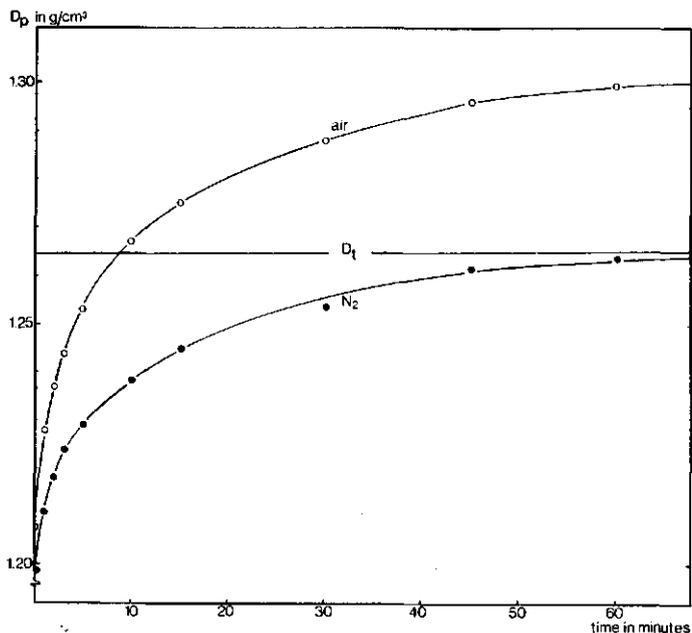
Fig. 2. Apparent mean particle density Dp of spray-dried whole milk in relation to time as observed by the Beckman pycnometer with air and nitrogen as the displacement gas. Dt = true density.

that of nitrogen. In 10 min 0.10–0.15 ml of nitrogen at atmospheric pressure dissolved in 2.0 g of butterfat.

The penetration rate of nitrogen into particles of spray-dried whole milk in relation to time was determined and the results obtained five powdersamples are shown in Fig. 3. These results demonstrate that Eq. 16 cannot be applied to describe the behaviour of the powder sample as a whole. A straight line is only obtained after 15–20 min.

A simple explanation of the curves in Fig. 3 may be that in the first 15 min the compressed gas rapidly fills the vacuoles of the more porous small particles. After that time the vacuoles of the larger particles with a considerably lower porosity are filled gradually.

Berlin and Pallansch (4) concluded from their results that the penetration of gases into milk powder particles cannot be described by Poisseuille's law, but that the surface diffusion along the pore walls dominates the flow of gas into spray powder particles. From the large difference in penetration rate between He and N_2 they also concluded that the pores in milk powder particles have molecular dimensions. This may be true in their case, but we frequently

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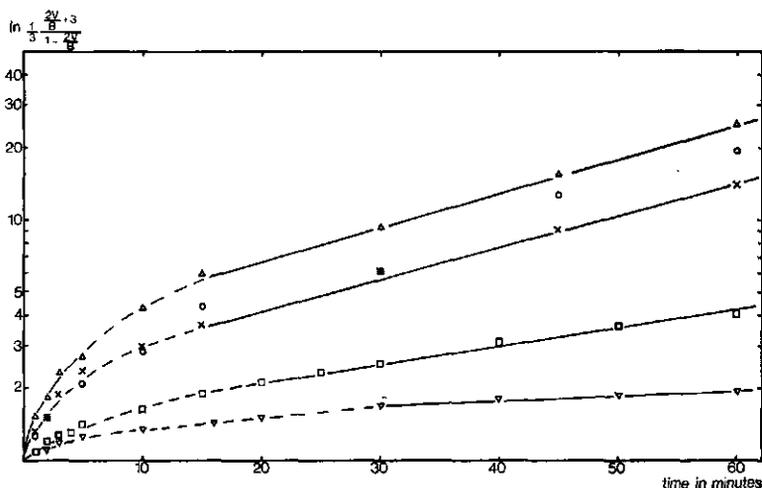
Fig. 3. Experimental check of Eq. 16 with five whole milk spray powders.

observed much higher penetration rates than they did, so that in those cases much wider pores or cracks must be present. Thus the conclusion of Berlin and Pallansch may not generally be correct.

The purpose of the theoretical treatment in 7.2 was to obtain a mean particle porosity γ, representative of a powder sample. Fig. 3 shows that this is not possible. To obtain a practical measure of the total particle porosity of a sample of spray dried whole milk we now introduce the porosity factor γ_{10}, which is the volume V_{10} of nitrogen which has penetrated into the particles during 10 min, divided by the available total vacuole volume B of the sample.

Thus: $\gamma_{10} = V_{10}/B$.   (18)

The rather arbitrary time of 10 min was considered short enough for absorption or adsorption of nitrogen to be negligible in most cases.

In the following we shall consider the correlation between particle porosity as defined above and the free-fat content obtained by a 10-min extraction at room temperature. The results obtained with the 7-hours Soxhlet extraction at 44°C seem not to be relevant in this case, but for completeness we will mention the data.

8.4 Free-fat content and particle porosity of spray-dried milk

From the milk powders available we selected a number with various free-fat contents. The fat content of the pilot plant powders numbered 11–18 varied from 25–35%, and the moisture content of most samples was less than 3.0%.

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Powders with equal fat contents were prepared from the same batch of concentrated milk. Only the samples marked with a C were manufactured by a centrifugal spray-drying process. All the others were prepared by pressure spray drying as described earlier (5). Main and cyclone fractions were collected separately and are marked with a and b, respectively. Five normal commercial whole milk spray powders were included (5, 29–32).

Free-fat content was determined by two different methods as reported earlier (6) viz by a 10-min extraction at room temperature and a 7 hours extraction at 44°C in a Soxhlet apparatus. In both cases petroleum ether (b.p. 40–60°C) was the solvent. The mean particle porosity γ_{10} was estimated as described in the preceding section.

Results obtained with the above powders are shown in Table 1. A cursory examination of these results shows that there is a strong correlation between the particle porosity γ_{10} and the free-fat content (10 min, 22°C) of spray-dried

Table 1. Free-fat content of whole milk powders in relation to the penetration rate of nitrogen into the powder particles γ_{10}.

Sample No	Fat (%)	Moisture (%)	Spec. gravity		B (%)	γ_{10} (%)	Free-fat content	
			D_t	Dp			10 min 22°C	7 h, 44°C
11a	25.7	1.9	1.28	1.13	12	2	3.1	13.0
11b	25.7	1.8	1.28	1.20	6	32	34	44
12a H	25.7	1.7	1.28	1.15	10	2	1.5	1.5
12b H	25.7	1.5	1.28	1.20	6	11	7.1	7.4
13a	30.3	1.2	1.26	1.10	12	4	8.7	47
13b	30.0	1.7	1.26	1.20	5	66	61	74
14a H	29.7	2.7	1.26	1.14	10	0	1.1	1.3
14b H	29.8	2.0	1.26	1.20	5	8	6.1	6.7
C15a	29.9	2.0	1.26	0.89	30	1	10.4	33
C15b	29.8	1.7	1.26	0.97	23	59	79	79
C16a H	30.1	1.5	1.26	0.91	27	1	1.0	1.1
C16b H	30.1	1.7	1.26	0.99	20	15	6.6	6.7
17a	35.5	1.8	1.24	1.00	21	9	8.4	59
17b	35.1	2.2	1.24	1.19	4	84	73	84
18a H	34.9	3.3	1.24	1.15	8	2	1.9	2.0
18b H	35.2	2.7	1.24	1.17	6	10	10.0	12.3
5	27.8	2.4	1.27	1.16	8	13	13.1	—
29	27.9	4.6	1.26	1.23	3	77	54	72
30	27.9	3.5	1.27	1.17	8	34	16	21
31	26.8	1.9	1.27	1.23	4	29	25	51
32	26.8	3.1	1.27	1.20	5	8	10.2	19

whole milk. A statistical analysis of the results yields a correlation coefficient $r = 0.94$. The residual variance is only 12% of the spread in the free-fat content or expressed otherwise, 88% of the spread in the free-fat content can be ascribed to the porosity of the powder particles as determined above. This strong correlation indicates that the particle porosity of spray dried whole milk is of major importance in the extraction of milk fat from such powders.

The regression equation appeared to be:

$$f = 0.87 \gamma_{10} + 1.2 \tag{19}$$

According to Eq. 19 only a small part of the fat can be extracted in 10 min at room temperature if $\gamma_{10} = 0$. This fat, probably originating from surface fat and fat globules situated in the surface layer of the powder particles amounts on the average to 1.2%. The factor 0.87 in Eq. 19 is complicated and difficult to interpret.

Results with powders prepared from concentrated milk homogenized in a Rannie homogenizer at 200 kg/cm², and marked H in Table 1, show that this homogenization considerably decreases both particle porosity and free-fat content regardless of whether the milk was spray-dried by pressure nozzles or by a spinning disk. Evidently, homogenization of the concentrated milk results in less porous powder particles.

The particle porosity as well as the free-fat content of the small particle cyclone powder fractions is in all cases much higher than that of the corresponding main fractions, in agreement with earlier observations (1,3).

A residual variance of 12% implies that in some cases the free-fat content does not agree so well with the particle porosity γ_{10}. If the free-fat content is too low (Samples C16b, 29, 30), this can be explained by assuming that on the average only a few relatively wide capillaries connect the vacuoles with the outer particle space. Consequently only a small number of fat globules inside the powder particles can be reached by fat solvents.

If on the contrary the free-fat content is too high compared with the particle porosity (Samples C15a, C15b) two explanations are possible:
1. The particles are more or less porous, but the pores, cracks or folds do not connect the vacuoles with the outer particle space. γ_{10} is thus small, but many fat globules are accessible to fat solvents;
2. A considerable part of the free fat consists of surface fat or of fat globules in the surface layer of the powder particles. In the latter case the size and the spatial distribution of the fat globules may be important. If, for example, the fat globules in the outer layer of the powder particles are dissolved by the solvent fat globules further inside can be reached through the 'holes' left by the outer ones.

Clustering or clumping of fat globules may greatly contribute to such a

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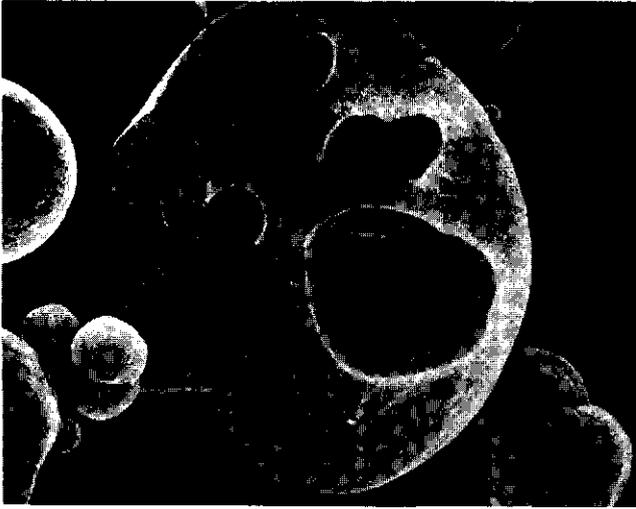
Fig. 10. Internal structure of a particle with several vacuoles prepared from homogenized concentrated milk (Sample 12a). The cut was made with a razor blade. Magnification × 3000.

pared from unhomogenized concentrated milk (Fig. 8) compared with that of particles prepared from homogenized concentrated milk (Fig. 9). The holes in the fracture surface are much smaller in the latter case. Probably most of these holes were occupied by fat globules, for the holes have approximately the corresponding size, which is different in the two samples.

Finally Fig. 10 shows a cross section of a powder particle containing several smaller vacuoles. The smooth cut was made with a razor blade.

Although the above photographs support the results shown in Table 1, they do not definitely prove the existence of pores or cracks connecting the particle interior with its surface.

Electron microscopic investigations of the internal structure of milk powder particles are now in progress by means of the freeze etching technique described by Buchheim (11). Here again no water is used for the preparation of the samples.

8.6 A possible explanation of particle porosity

Until now the question has been unanswered why powders prepared from unhomogenized concentrated milk have a higher particle porosity than those from homogenized concentrated milk, and why small particles have a higher porosity than the larger ones in the same powder.

When searching for an explanation a few earlier observations (1, 2, 3, 10) must be taken into account:

1. The particle porosity of spray-dried skim milk, of spray-dried lactose and of spray-dried whey is very small regardless of the particle size. Spray caseinate particles on the contrary are very porous (2).

2. Many particles of spray-dried skim milk and of spray caseinate show deep surface folds under the microscope, whereas these are not usually observed in particles of spray-dried whole milk, spray dried whey and spray lactose (10).

3. Moisture absorption by spray-dried whole milk results in a considerable decrease of the amount of free fat. The effect is reversible, which indicates that the the pores or cracks in the particles close or re-open due to the swelling and shrinkage, respectively, of the powder material during the absorption or desorption of moisture (3).

Surface folds, pores and cracks are the result of mechanical stresses caused by uneven drying of the material in different parts of the powder particles. Probably the shrinkage of the casein on drying plays an important rôle as indicated by the above observations. Amorphous lactose evidently does not contribute to the formation of folds or cracks. Fat globules, the volume of which is unaffected by drying, may hinder the shrinkage of the casein and the more so, the larger the fat globules are in comparison with the powder particles.

Shrinkage and cracking of drying material are old problems in the ceramic industry. Research in this field yielded the following conclusions (12, 13). Crust formation and cracking are promoted by a high drying rate. The risk of cracking is low if the percentage of 'inert' particles < 2 μm exceeds 33 % and the shrinkage percentage is 7.5 % or more. Evidently shrinkage prevents cracking.

Our results appear to be in agreement with these conclusions. On the average the surface to volume ratio of the small particles of the cyclone fractions is twice that of the corresponding main fractions (1, 3). Consequently the evaporation rate and thus the risk of cracking in the small particles of the cyclone fractions is considerably higher than in the larger particles. An indication of the higher drying rate is that the drying temperature of the small particles as derived from the β/α ratio of the lactose is on the average 20°C lower than that of the corresponding large particle fractions (2).

Homogenization of the concentrated whole milk results in a considerable size reduction of the fat globules which are the 'inert' particles in our case. In contrast with the rigid clay particles, fat globules are plastic at room temperature and some deformation may occur by stresses in the powder particles. E.M. photographs of the fracture surface of broken particles show holes, which indeed often have a shape deviating more or less from a sphere, as can be seen
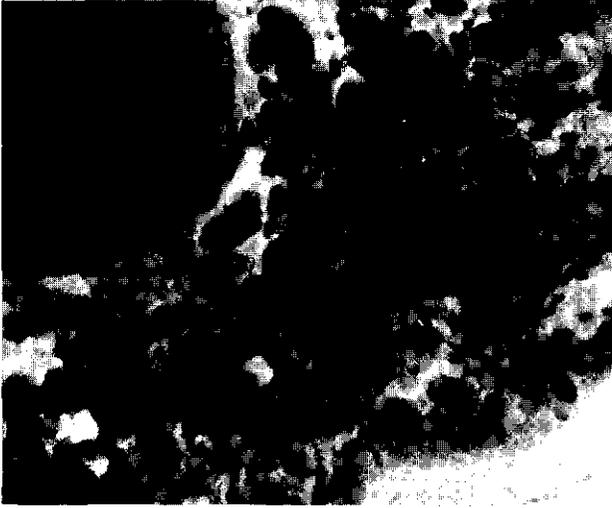
Fig. 11. Fracture surface of a broken particle (Sample 11b). Magnification × 5000.

in Fig. 11 and 12. As will be shown in a subsequent paper the major part of the fat globules in powders prepared from homogenized concentrated milk have diameters below 2 μm, whereas powders from unhomogenized concentrated
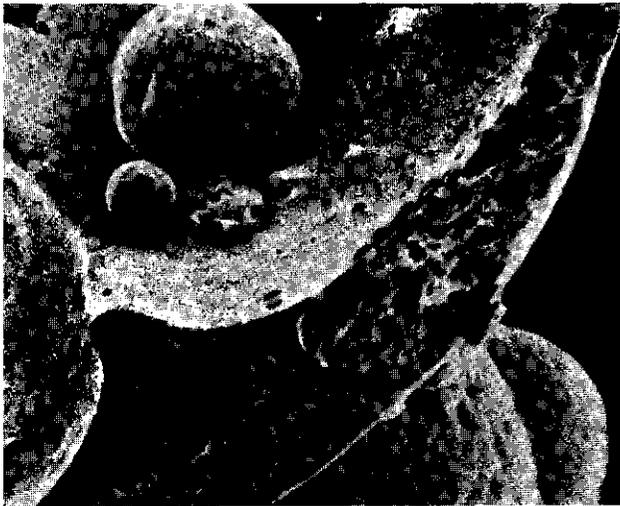

Fig. 12. Fracture surface and internal surface of vacuoles of a broken powder particle (Sample 11b). Magnification × 2500.

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milk contain many fat globules of 3 and 4 μm. This can also be concluded from Fig. 8 and 9. Such large fat globules may locally prevent the casein from shrinking evenly, with cracking as a result. Probably this is the reason that the porosity of powder particles from unhomogenized milk is higher than those from homogenized milk.

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9. The size distribution of fat globules in concentrated milk and in spray-dried milk

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Abstract

The fat globule size distribution in concentrated milk, and in milk reconstituted from spray powders prepared from it, were investigated by means of a Coulter counter. Moreover the size distribution of the fat globules in reconstituted milk from five other spray powders, varying considerably in their content of free fat, was also determined. From the results, the following conclusions were drawn. Spraying of concentrated milk causes a considerable size reduction of the fat globules, and this effect increases as the pump pressure or the speed of the spinning disk increases.

Some coalescence of fat globules takes place during drying or during reconstitution of milk from powders, particularly if the concentrated milk was not homogenized.

The good agreement between the percentage of fat present as fat globules $> 2 \mu m$ in milk reconstituted from five powders and the increase of the percentage of the fat extracted from the powders with extraction time and temperature, suggests a relationship between these two quantities. A possible explanation is given for the observed phenomena.

9.1 Introduction

Free fat in spray-dried whole milk must consist partly of fat globules situated in the surface layer of the powder particles, because such fat globules can be reached directly by fat solvents. The contribution of these fat globules to the total amount of free fat may depend on the size distribution of the fat globules in the powder particles.

The size distribution may also be important in connection with an effect which we mentioned earlier (1), viz the possibility that fat globules in the interior of the powder particles can be attained by fat solvents via the holes left by the fat globules in the outer layer of the powder particles. This may occur particularly when the fat globules are clumped or clustered and are larger.

There are some data on the size distribution of the fat globules in milk reconstituted from spray-dried whole milk (2, 3). It was shown by Blaauw (2)

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that when fresh milk containing 48.5% of the fat globules with diameters < 2 μm, is concentrated in a long-tube vertical film evaporator to 35% or 50% total solids, the percentage of these fat globules increased to 76.5% and 87%, respectively. Further size reduction was caused by spray drying with a spinning disk as well as with pressure nozzels. The percentage of fat globules with diameters < 2 μm then increased to 95–98.5%. Details concerning the manufacturing process or the determination of the size distribution were not given.

We determined the size distribution of the fat globules in concentrated milk and investigated the influence of homogenization, the pump pressure and the speed of revolution of the spinning disk when spray drying. In addition, the size distribution of the fat globules in milk reconstituted from spray-dried whole milk was determined.

The results are shown in the following sections.

9.2 Methods

The fat globule size distribution was studied by means of a Coulter counter model FN with a 50-μm orifice tube. The counting technique and its limitations have been described by Walstra and Oortwijn (4). For practical reasons we were not able to apply the right coincidence corrections as proposed by these authors, but used the corrections recommended in the instruction manual of the counter. In our case this may be sufficient as we in fact are more interested in the relative size distributions of the fat globules than in the absolute size distributions.

Preparation of the samples was carried out in a similar way as reported by Walstra et al. (5). The total solids concentration of the counting 'solution' was equal to a 10^{-4} dilution of fresh milk. The instrument was calibrated with puff-ball spores. All measurements were carried out at least in duplicate.

A batch of fresh milk was concentrated in a vertical film evaporator to a total solids content of 40% and divided into three equal parts. One part was pumped at pressures of 100 and 200 kg/cm², respectively, through a spray nozzle 69/21 (Spraying Systems). The other part was fed into a spinning disk atomizer with a diameter of 16.0 cm. Two speeds were applied: 12000 and 20000 rpm. In all cases the concentrated milk was pasteurized at 72°C. Samples were taken from the concentrated milk before pasteurizing and after atomizing, the latter in a sample cup at a distance of 10–20 cm from the spray nozzle or the spinning disk. The third part of the concentrated milk was homogenized in a Rannie homogenizer at 200 kg/cm² and sprayed with a nozzle at a pressure of 100 kg/cm². Samples were taken as above.

Another batch of fresh milk was concentrated as above and divided into

two parts, of which one was homogenized (200 kg/cm²). Both parts were then spray-dried with a nozzle, applying a pump pressure of 100 kg/cm². Samples were taken from the sprayed milk at 10 cm from the nozzle and from the main and cyclone fractions of the powders.

In all of the above samples of concentrated milk and powders, the fat globule size distribution was determined with the Coulter Counter. The samples were reconstituted in water of 50°C to a fresh milk concentration before further dilution to a 10^{-4} concentration for counting.

Finally five whole milk spray powders differing in free-fat content were reconstituted and treated as above to investigate a possible relationship between fat globule size and free fat. The five powders were the same as used for other investigations described earlier (6).

9.3 Results and discussion

The results are presented as cumulative fat globule size distributions in Fig 1–3. According to Fig. 1 milk concentrated in a vertical film evaporator contains a considerable number of fat globules in the size range 3–5 μm. This was confirmed qualitatively by microscopic observations which also showed that the number of fat globules with diameters of 7–10 μm is not negligible, which is in agreement with several other observations.

Spraying of the concentrated milk causes a considerable size reduction of the fat globules, and the more so as the pump pressure or the speed of the spinning disk increases. Pressure spraying is much more effective in this respect than disk spraying. In fact we found that the size distribution in concentrated milk homogenized at 200 kg/cm² with a Rannie homogenizer is almost equal to that in milk sprayed with a nozzle at the same pressure. This can be concluded from Curve 5 in Fig. 1.

In previous reports (1, 6, 7, 8) we differentiated between spray-dried whole milk prepared from homogenized and unhomogenized concentrated milk. The above results show that such a differentiation is somewhat misleading because spraying causes considerable homogenization. However, because we homogenized at 250 kg/cm² and spray-dried with pressures of 60 kg/cm², this implies that we obtained powders greatly differing in fat globule size distribution. Thus it would be better to speak of powders prepared from strongly and weakly homogenized concentrated milk.

Fig. 2 shows that the fat globule size distribution in milk reconstituted from powders prepared from homogenized concentrated milk is almost the same as that of the concentrated milk itself. If the concentrated milk is not homogenized in a Rannie homogenizer, the reconstituted milk contains more large fat glo-

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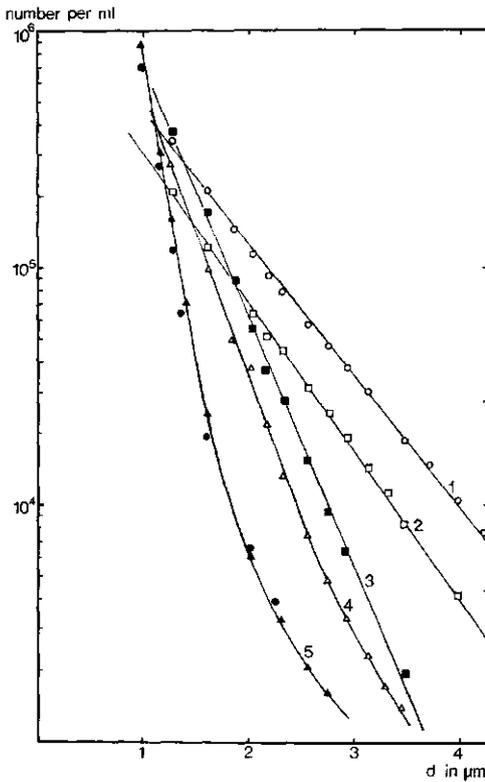
Fig. 1. Cumulative size distributions of fat globules in concentrated whole milk with 40% total solids.
○ ● from the evaporator; ○ unhomogenized; ● homogenized at 200 kg/cm²
□ after spraying with a spinning disk; 12.000 rpm
■ after spraying with a spinning disk; 20.000 rpm
△ after spraying with a pressure nozzle; p = 100 kg/cm²
▲ after spraying with a pressure nozzle; p = 200 kg/cm².

bules than does the original concentrated milk. It is not possible to differentiate between a coalescence of fat globules during drying or during reconstitution of the powders, nor is it possible to distinguish between large fat globules and clusters or clumps of fat globules passing the orifice of the Coulter counter. There is no indication that milk reconstituted from the cyclone fractions contains more large fat globules than does milk from the corresponding main fraction of the powders.

Fig. 3 shows the fat globule size distributions in milk reconstituted from five spray powders used in an earlier investigation (6). The size distributions differ considerably. To make some quantitative measure of the amount of fat present as large fat globules, we rather arbitrarily calculated the percentage of fat present as fat globules with diameters > 2 μm. The results are shown in Table 1, together with the percentages of the fat extracted with petroleum ether from the powders in 10 minutes at 22°C and in 20 hours at 40°C (6).

A comparison of these results shows that there is no agreement between the

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number per ml
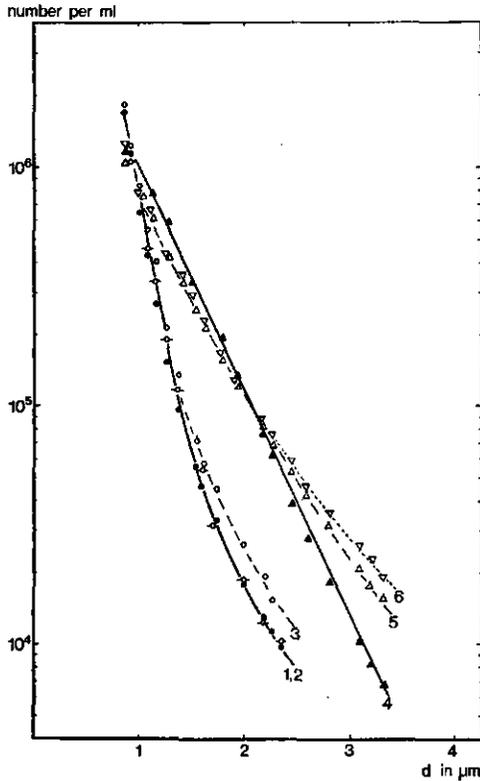
Fig. 2. Cumulative size distributions of fat globules in concentrated milk (40% total solids) and in milk reconstituted from spray powders prepared from the concentrated milk by spray drying with a pressure of 100 kg/cm².
1 = concentrated milk homogenized at 200 kg/cm²
2,3 = milk reconstituted from powders prepared from 1; ● cyclone fraction; ○ main fraction.
4 = unhomogenized concentrated milk.
5, 6 = milk reconstituted from powders prepared from 4; 5 is the main fraction, 6, the cyclone fraction.

amount of fat extracted in 10 minutes and the percentage of fat in globules > 2 μm. The agreement is better if the amount of fat extracted in 20 hours at 40°C is considered. A rather good correlation is obtained if the difference in the percentage of fat extracted by the two methods (Table 1) is compared with

Table 1. The percentage of fat extracted by two methods from five whole milk spray powders and the percentage of fat present as fat globules with diameters > 2 μm.

| Sample number	Percentage of fat extracted			Percentage fat in globules > 2 μm
	10 min 22°C	20 h 40°C	difference	
1	1.6	2.5	0.9	0.3
2	9.9	10.1	0.2	0.6
3	8.0	14.2	6.2	11
4	9.1	25	15.9	15
5	16.8	59	42.2	27
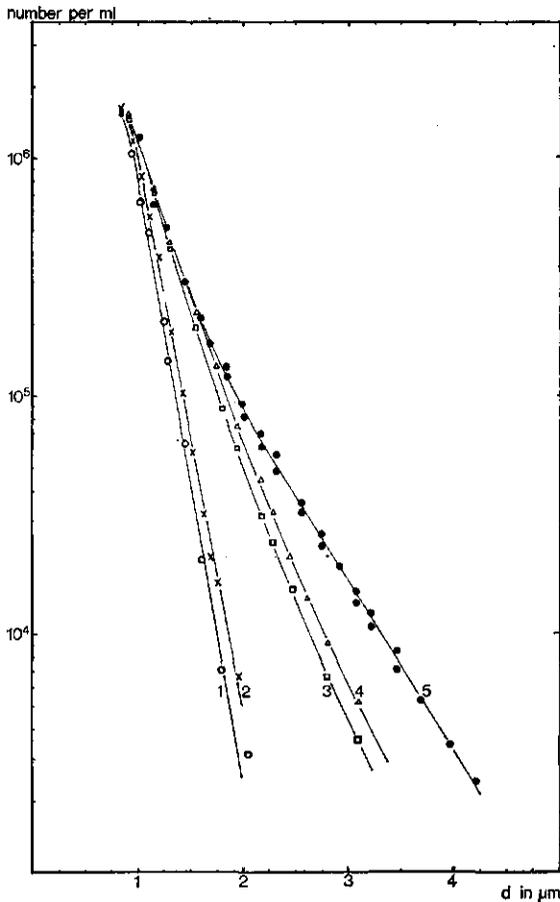
Fig. 3. Cumulative distributions of fat globule size in milk reconstituted from pressure-spray-dried whole milk. Powder samples 1 and 2 were prepared from strongly homogenized concentrated milk; 3,4 and 5 were normal commercial powders.

the amount of fat present as fat globules with diameters $> 2 \mu$m. A similar correlation is obtained if the lower limit of the large fat globules is assumed to be higher. As an illustration, the figures shown in Table 1 are the best in our opinion. In spite of the small number of observations, the above results suggest that there is a relationship between the increase with time and temperature of the amount of fat extracted from spray-dried whole milk and the number of large fat globules.

Earlier (1) we reported that there is a strong correlation between the percentage of the fat extracted in 10 minutes at room temperature and the mean particle porosity of the powders.

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cannot gain access to such fat. A similar explanation was given by Coulter et al. (3) who assumed that the continuous phase of spray-dried whole milk is impenetrable to fat solvents.

King agreed with Holm et al. and summarized his conclusions as follows (4): Fat in dried milk can occur either in a finely emulsified state or in a coalesced de-emulsified state. In the latter case the membrane around the fat globules has been damaged or entirely removed, with the result that the globules are apt to flow together to form 'pools' of fat. Such fat is extracted with fat solvents and was designated by Holm et al. as 'free fat'. In a subsequent paper (5) he suggested that the unprotected fat permeates the dried milk particles and that part of it reaches the surface, rendering it water-repellent. Many authors (see Ref. 6) agreed with King and considered free fat as consisting mainly of surface fat on the particles, either as surface layer or as patches on the particle surface.

The present report deals with the results of experiments to estimate the amount of surface fat on the particles and results are given of a duplication of the experiments which led Holm et al. to their conclusions. The earlier theories assuming that free fat consists of fat globules with damaged or entirely removed membranes has now been checked experimentally.

Taking into account our earlier results (7–14), a physical model for free fat in spray dried whole milk is proposed and the practical consequences discussed.

10.2 Surface fat on spray powder particles

Undoubtedly there is a certain amount of fat present on the surface of particles of spray dried whole milk. This was proved by Electron microscopic photographs (10, 15) as well as by cohesion measurements. The only question is, how much extractable fat is surface fat.

The dissolving of the free fat from the surface of powder particles must be a rapid process. This can be demonstrated by a simple experiment. If 1 g of anhydrous butterfat is distributed in about 25 small portions on the bottom of a 250 ml glass beaker, the fat can be dissolved quantitatively in 1 1/2 minutes in 100 ml petroleum ether at room temperature by continuously swirling by hand. Dissolution of the fat can be estimated visually as well as by determining the amount of fat in the solvent.

A related experiment was carried out as follows. A microscope slide was coated with a layer of anhydrous butterfat, about 5 μm thick. The thickness was determined by weighing. Such a fat layer can be dissolved within 10 seconds by a fat solvent at 20°C.

In all of our free-fat determinations we used 2.5 g of whole milk powder (7). This amount of powder has a surface area of the order of magnitude of 3000

cm² (8). It contains about 0.700 g of fat and thus, if all this fat were spread out as an even layer on the powder particle surface, its thickness would be about 2 μm. And, as shown above, such a thin fat layer would dissolve in a fat solvent within a few seconds.

However it seems rather unlikely that the surface fat is present as an even layer on the powder particles. It is more probable that the surface fat consists of patches or accumulations of fat in surface folds or at contact points between the particles as shown, for example, in E.M. photographs (10, 15) and by Pyne (16). Such a deposit of fat would still dissolve in a short time, e.g. 5–20 seconds in a fat solvent at room temperature.

In an earlier report (7) we showed that the amount of fat extracted in 1 minute from spray-dried whole milk is sometimes much larger than the amount obtained with a contact time of 10 seconds. Later on (13) it was shown that from several whole milk spray powders 60 to 80 % of the fat could be extracted in 10 minutes at room temperature, and it is hard to believe that all this fat is located on the particle surface.

The above results would indicate that the amount of surface fat must be estimated by an extraction for 10 seconds or less at 20°C, but even with such short extraction times it is possible that part of the extracted fat is not surface fat. Thus, although it is clear that in many cases only a minor part of the free fat is surface fat, there is no way of determining it separately.

It needs no further comment that, in our opinion, an extraction time of 15 minutes for the determination of the surface fat, as proposed by Písecký (17), is definitely too long.

10.3 The relationship between fat content and free-fat content

Holm et al. (1) observed that the amount of fat that can be extracted from spray-dried milk increased sharply with increasing fat content at 24–26 % fat. Homogenizing the concentrated milk yielded spray powders with lower free-fat contents, but the increase still occurred at about the same fat content.

We studied the relationship between free fat content and total fat content of spray-dried milk with four series of powders varying in fat content from 10 to 60 %. The preparation of the powders was described in an earlier paper (8). At each fat level four powders were obtained from the same concentrated milk as follows. The concentrated milk was divided into two parts. One part was homogenized in a Rannie homogenizer at 250 kg/cm² prior to spray drying and the other part was not homogenized. Main and cyclone powder fractions were collected separately from the drier. In this way we obtained four powders with the same total fat content but differing considerably in free-fat content.
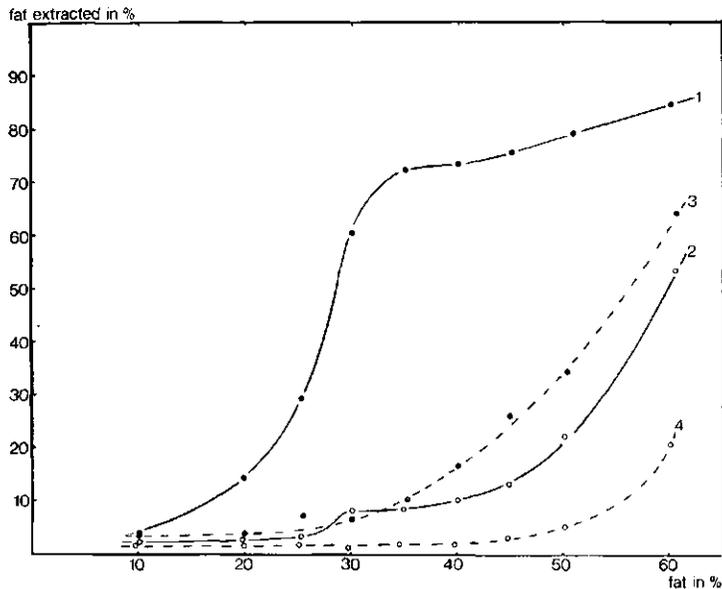
Fig. 1. The percentage of fat extracted from spray-dried milk in 10 minutes at 22°C in relation to the total fat content; 1 and 2 are cyclone and main fractions, respectively, of powders from 'unhomogenized' concentrated milk; 3 and 4 are cyclone and main fractions, respectively, of powders from homogenized concentrated milk.

According to our usual procedure we determined the free-fat content of the powder by a 10-minute extraction at room temperature as well as by a 7-hour Soxhlet extraction at 44°C (7).

The results of the cold extraction are presented in Fig. 1. They show that the sharp increase in the amount of free fat between 25 and 30% of fat occurs only with the 'unhomogenized' cyclone powder fractions. The amount of fat extracted in this way from the other powder fractions increases more gradually with the fat content and lies rather in the range of 30–60% fat.

Fig. 2 shows the results of the 7 hours Soxhlet extractions. Here the amount of free fat increases strongly with the fat content between 20 and 30% for both the main and the cyclone fractions of powders prepared from "unhomogenized" concentrated milk. Such a sharp increase occurs with powders prepared from concentrated milk which was homogenized prior to spray drying only at a fat content of about 40%.

Thus in general the conclusion of Holm et al. (1) is not confirmed and probably only applies to special cases. Normally some considerable homogenization takes place during pressure spray drying, as we showed in a preceding

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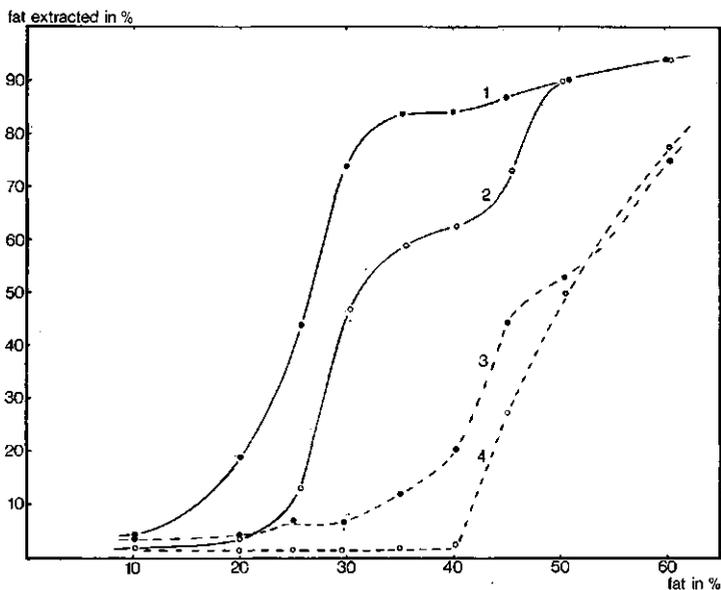
Fig. 2. The percentage of fat extracted from spray-dried milk in 7 hours at 44°C in relation to the total fat content. The numbering of the curves is the same as in Fig. 1.

report, so that the leap should occur at about 40 % fat, rather than at 25 % of fat according to Holm et al. (1). Later in this paper, a qualitative explanation of the curves in Fig. 1 and 2 will be given.

10.4 Free fat and the fat globule membrane

Several workers (see Ref. 6) explained the occurrence of free fat in milk powder by assuming that such fat consists of fat globules in which the protein membranes which protect the fat globules in fresh milk are either damaged or absent. In an earlier report (6) we doubted this view for two reasons.

First, the fat globules in milk powder particles have been subjected to a number of processing steps which have damaged all or the major part of the native membranes. These steps are: pasteurizing, concentrating and spray drying. In particular, the considerable homogenization caused by pressure spray drying is of relevance. Secondly, it seemed rather unlikely that a dry fat globule membrane with a thickness of 5–10 nm, consisting of about 50 % of lipids, would give more protection against fat solvents than a far thicker layer of non-fat milk solids in the powder particles.

To investigate this problem we manufactured a number of spray powders

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with particles only consisting of lactose and fat globules, i.e. without protein membranes. The powders were prepared from a suspension of purified anhydrous butterfat in a concentrated lactose solution.

A fairly stable suspension with 40% solids and various fat contents was obtained by homogenizing the mixture three times with a Rannie homogenizer at a pressure of 250 kg/cm². To improve the emulsification we added glycerine monostearate equivalent to 0.5% of the fat. Drying conditions were similar to those described earlier (8) for the series of whole milk powders. Main and cyclone fractions were collected separately as usual. We made a range of powders with varying fat contents in this way.

Free-fat contents of the powders were determined by the cold extraction method (7). The results, shown in Fig. 3, demonstrate that at a fat content of 30% the free-fat content is on the average 20% of the fat in the cyclone fractions and about 10% in the main fractions. The free-fat content of the cyclone fractions increases considerably with the fat content between 30 and 50% fat, but that of the main fractions only increases if the fat content exceeds 40%.

These results show that fat globules without a protein membrane or other coating can be protected against fat solvents by the amorphous lactose. On the other hand, in milk the hydrophobic fat globules are coated with some surface-active material which is present in the milk. Eggmann (18) and Henstra and
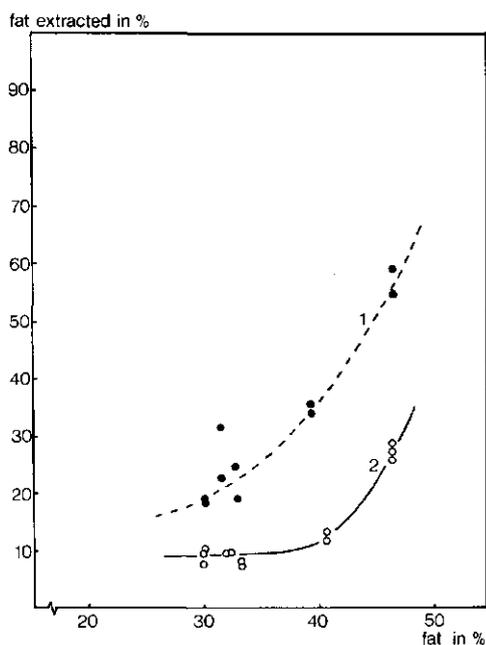

Fig. 3. The percentage of fat extracted in 10 minutes at 22° C from spray-dried lactosefat suspensions in relation to the total fat content; 1 = cyclone fractions; 2 = main fractions.

Schmidt (19) observed that the fat globules in milk may be partly covered by casein. It is possible that such a coating in a dry state provides a certain resistance against penetrating fat solvents. Because experimental evidence concerning the protective function of a fat globule membrane or another sheath around the fat globules in dry milk particles is lacking — and theoretically this is rather unlikely — the theories of Holm et al. (7) and of King (4, 5) have to be rejected for the time being.

10.5 A model for free fat in spray-dried whole milk

In the preceding sections we objected to earlier explanations for the occurrence of free fat in spray-dried whole milk. In their stead we gradually developed a physical model in the previous papers in this series (8, 9, 10, 11, 13, 14) which could explain most of the phenomena observed until the present time. The model agrees with the earlier view of Coulter et al. (3) that the continuous phase of spray-dried whole milk, i.e. the dry milk serum material, is in principle impenetrable to fat solvents.

Summarizing our earlier conclusions and suggestions, we propose the following model, based on the accessibility of the fat in particles of spray dried whole milk to fat solvents.

Extractable fat (f_e) in principle consists of four 'components':

$$f_e = f_s + f_l + f_c + f_d \tag{1}$$

1. $f_s = $ *surface fat* present as pools or patches of fat on the powder particle surface particularly in surface folds and at contact points between the particles;
2. $f_l = $ *outer layer fat*, consisting of fat globules in the surface layer of the powder particles, which can be reached directly by fat solvents;
3. $f_c = $ *capillary fat* consisting of fat globules inside the powder particles which can be reached by fat solvents via capillary pores or cracks;
4. $f_d = $ *dissolution or 'second echelon' fat* consisting of fat globules inside the powder particles which can be reached by fat solvents via the holes left by dissolved fat globules in the outer particle layer or close to wide capillaries in the powder particles.
Fig. 4 illustrates our model.

The above distinction between different forms of extractable fat seems to be somewhat artificial, but it has practical relevance. Surface fat probably consists of patches or pools of coalesced fat. During reconstitution of the powders to liquid milk such fat will probably further coalesce into a small number of relatively large fat globules or fat clumps, in contrast with the other forms of extractable fat, which yield fat globules in the reconstituted milk of the same

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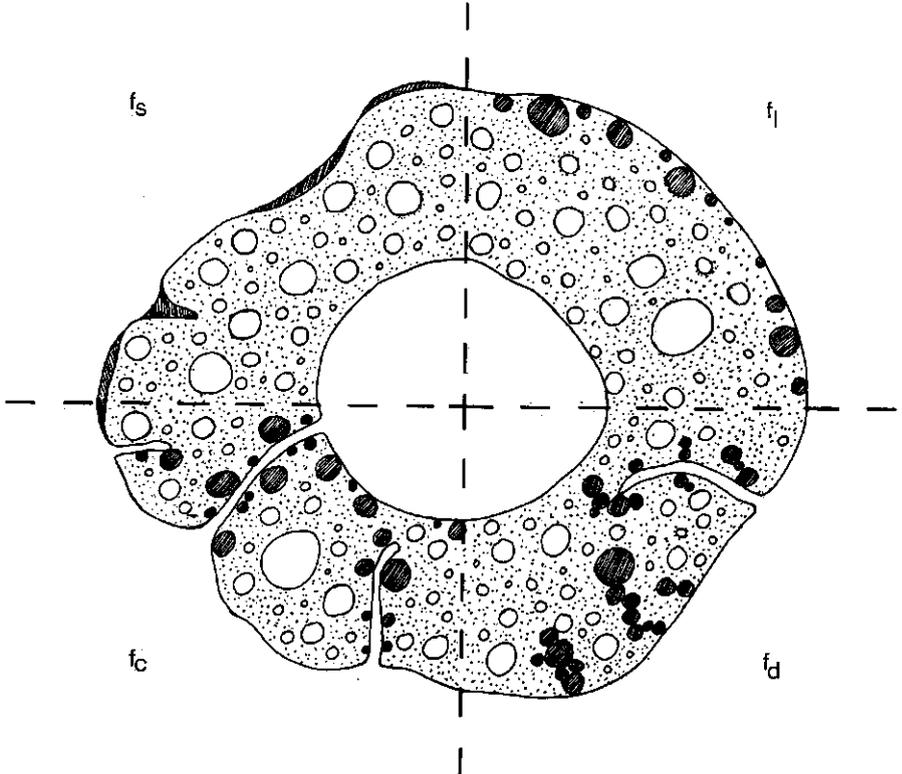
Fig. 4. Schematic model of four forms of extractable fat in a milk powder particle with a central vacuole. The dark areas represent extractable fat.

size as present in the powder particles. A differentiation between f_s and f_l is necessary because f_s may influence the surface properties of the powder particles such as the cohesion and the wettability, whereas f_l does so to a much lesser extent, if at all.

In some cases (13) we observed a strong increase with time in the amount of fat extracted from powders with a relatively low particle porosity. This may be due to a dissolution of fat globules in the interior of the powder particles via the holes left by fat globules dissolved in the outer layer. Such a process seems to be rather slow compared with the penetration of fat solvents in capillaries and subsequent dissolution of fat globules contiguous with the capillaries. As we reported earlier (13), 60–80 % of the fat can be extracted from relatively porous powder particles in 10 minutes at room temperature. Thus an extraction via the capillaries must be a relatively rapid process. These observations led us to distinguishing between f_c and f_d.

While the conceptional difference between the four fractions of f_e is simple,

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a clear cut experimental differentiation is much more difficult. In practice unfortunately only a rough differentiation can be made.

Surface fat f_s is extracted in a short time e.g. 10 seconds or at most 1 minute, but even in that short time, fat represented by f_l and f_c may contribute to f_e.

An extraction at room temperature for 10 minutes probably yields mainly the extractable fat represented by $f_s + f_l + f_c$. Prolonged extractions, particularly at temperatures considerably above room temperature, yield an additional amount of fat due to the contribution of second-echelon fat represented by the term f_d.

The extraction of a component from the interior of powder particles is a general problem in chemical industry, and several authors have tried to solve it theoretically, particularly the extraction via capillaries. The rather complicated theoretical equations derived by Piret et al. (20) and by Romankov et al. (21) can only be checked by experimental results obtained with model systems. Liebhafsky (22) showed that for f_c values below 50 %, the extraction process via capillaries can be described by a simple equation

$$
f_c = 2 \left(\frac{\pi \cdot D_l \cdot t}{l^2} \right)^{1/2} \tag{2}
$$

D_l = the diffusion constant of the solvent
l = the length of the capillaries
t = the extraction time.

We tried to fit our experimental results obtained with porous powders, of which it might be expected that the contribution of f_c to f_e would be relatively large, to Eq. 2. These were the results obtained with extraction times ranging from 10 seconds to 20 hours shown in Table 4 of an earlier report (7). A plot of f_e against $\sqrt{t}$ yielded a straight line between $t = 10$ seconds and $t = 10$ minutes in only one case. In the other cases strongly curved lines were obtained. The reason may be that with very short extraction times the contribution of f_c to f_e is relatively small, whereas with intermediate extraction times f_e may consist mainly of extracted fat represented by f_c. It is probable that most capillary fat has already been extracted in 10–30 minutes (8). Longer extractions may only yield additional amount of second echelon fat represented by f_d.

A simple calculation shows that if the capillaries in the powder particles are cylindrical and Poiseuilles law is valid, the penetration speed of a fat solvent into a powder particle is

$$
\frac{dl}{dt} = \frac{\sigma r}{4 \eta \, l} \cos \vartheta \tag{3}
$$

l = the penetration depth.

σ = the surface tension of the penetrating liquid against air.

r = the capillary radius.

η = the viscosity of the penetrating liquid.

θ = the contact angle which is very small with the applied organic solvents. Integration yields:

$$l = \left(\frac{\sigma r}{2\eta} \cdot t \right)^{1/2} \tag{4}$$

At room temperature $\eta \approx 1/2$ cp and for organic solvents σ is about 20 dyne/cm. If the capillary diameter is 0.01 μm, the penetration depth after a contact time of 1 second is about 450 μm. Because most spray powder particles have diameters below 100 μm, fat globules in the centre can be reached by fat solvents within one second.

The fat transport from the interior of the powder particles to the surrounding liquid is governed in principle by a dissolution and a diffusion process, which is difficult to describe mathematically and to check experimentally. The same may be said of the dissolution of fat globules via the holes left by other dissolved fat globules. If more data were available concerning the pore size distribution and the spatial distribution of the fat globules in the powder particles, it might be possible to calculate the extraction of fat from such particles. At the moment we have to limit ourselves to qualitative considerations.

In the next section possible explanations of other earlier observations with the help of our model will be discussed.

10.6 Discussion of the relation between the fat content and the free-fat content

It is possible to explain most of the known phenomena with the proposed model. First we will consider the curves in Fig. 1 and 2 in this paper.

Curve 1 in both figures concerns the cyclone fractions of powders prepared from 'unhomogenized' concentrated milk. Particles of such powders not only have a relatively large surface area in comparison with the corresponding main fractions, but they are also highly porous and the more so as the fat content increases (13). The amount of surface fat f_s is in principle proportional to the fat content. This cannot explain the sudden increase of f_e in the range 20–30 % fat, and it is unlikely that the major part of the fat extracted in 10 minutes (70 % of the total fat) at a fat content of 30 % is surface fat. The same may be said of the outer layer fat f_1. Nevertheless the extraction must be a rather rapid process, and an extension of the extraction time from 10 minutes to 7 hours only slightly

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increases the amount of extracted fat. The strong increase in the amount of extractable fat must thus be ascribed mainly to the considerable increase in the particle porosity (13) between 20 and 30% fat, and a minor part to the increase of the amount of surface fat f_s.

Curve 2 in Fig. 1 and 2. Particles of the main powder fractions prepared from 'unhomogenized' concentrated milk are less porous (13) and the specific surface areas are about half that of the corresponding cyclone fractions. Consequently the contribution of the fat represented by the terms f_s and f_c to f_e is much less. The fat globule size distribution is almost the same in both powder fractions. The large difference in the amount of fat extracted in 10 minutes from the two powder fractions (Fig. 1, Curves 1 and 2), which may be considered equal in all other respects can thus be explained.

A comparison of Curve 2 in Fig. 1 and 2 shows that f_e increases strongly with increasing extraction time and temperature for the main powder fractions. Thus the fat in these powders is not easily accessible, which can be due either to the capillaries being relatively narrow or relatively few or to the fat later extracted, being mostly dissolution fat f_d. The second explanation is more probable, as is seen from the effect of homogenization. If we compare the main fractions with and without homogenization (Curves 2 and 4), we have two powders with a particle porosity of the same order of magnitude, but with a great difference in fat globule size. And thus the fact that powders prepared from unhomogenized concentrated milk, have a much higher free fat content, at least in the range of 20–60% fat (Curve 2 in Fig. 2), has to be ascribed to mechanism No 4 represented by f_d.

Curves 3 and 4 in Fig. 1 and 2 show the amount of fat extracted from powders prepared from homogenized concentrated milk. In general the particle porosity of such powders is rather small. Up to fat contents of 40% the curves are almost equal in both graphs but at higher fat contents the amount of fat extracted increases considerably with time and temperature. A special feature of Curve 4 in Fig. 2 is the steep increase at a fat content of 40%. Curve 3 also shows an increase, but less pronounced. A simple calculation shows that at approximately this fat content all fat globules inside the powder particles touch one another if the most open sphere arrangement is assumed. In practice the latter may not be the case but the probability that the fat globules touch each other increases strongly when the fat content exceeds 40%. Accordingly the situation becomes more favourable for fat solvents to reach fat globules in the interior of the powder particles via the holes left by the dissolved fat globules in the outer layers (Mechanism No 4). Such a process takes more time than an extraction via capillaries in the powder particles. As for Curve 4 in Fig. 1 and 2 mechanism No 4 applies.

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Our model, based on the accessibility of fat by fat solvents is physical in nature, so that the physical structure of the powder particles, namely the spatial distribution of the fat, the particle size and the particle porosity, plays a dominating role. The physical structure of the powder particles is formed during atomization and subsequent drying of the milk droplets. In this view all process steps prior to atomization except homogenization, which may cause physico-chemical changes in the milk, are of minor importance for the amount of extractable fat in the powders. Thus the contradictory results (6) concerning the influence of the forewarming temperature or the holding time of the milk on the free-fat content of the powders, must be ascribed to different drying conditions which, in most cases, were not mentioned. This influence of the drying conditions of spray dried whole milk has been reported earlier in this series (8). Its relevance to results reported earlier in the literature has been reviewed in Section 1.3 (6).

Summarizing these earlier conclusions, it may be said that spraying pressure as well as total solids content influences the particle size and thus the specific surface area and the amount of surface fat (8).

Considerable size reduction of the fat globules in the concentrated milk occurs during spraying, particularly if the spraying pressure or the rotation speed of the spinning disk is high (14), thus decreasing the amount of free fat extracted by mechanisms No 2 and 4. EM micrographs showed (12) that the drying conditions of the individual spray powder particles may differ greatly. And thus the temperature distribution in the drier may be important for the physical structure of the powder particles and for the amount of fat extracted from them.

Spray dried whole milk in which the lactose has been crystallized due to moisture absorption consists of highly porous particles as we showed earlier (23). The fat extracted from such powder particles must be represented by the term f_c in Eq. 1. A difference from normal spray dried whole milk is, that when the lactose has been crystallized, the major part of the fat globules inside the powder particles may have coalesced to larger units, thus influencing the properties of the milk reconstituted from such powders.

10.7 Practical consequences of the model

Several authors have reported correlations between the free-fat content of dried milk and other properties of practical importance, the latter having been summarized in an earlier report (6) as follows:
a. The oxidation flavour
b. The dispersibility or the wettability

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c. The rising of cream and foaming in the reconstituted milk

d. The stickiness of spray dried whole milk.

a. The oxidation flavour. It is natural to suppose that the fat which is in direct contact with oxygen from the air surrounding the powder particles is the first to oxidize. In our model this would be the surface fat, the fat globules in the surface layer and the fat globules touching the capillaries in the powder particles. On the other hand we showed (23) that the rate of exchange of oxygen in the powder particles is rather high in comparison with the development of the tallowiness. It is therefore not surprising that we found no correlation between the amount of fat extracted by the two methods we applied and the development of the oxidation flavour (9).

b. The dispersibility or the wettability. These powder properties can only be influenced by that part of the extractable fat which is located in or on the powder particle surface viz f_s and f_l. Thus a relationship between dispersibility and free fat would only be found if the extraction time were very short i.e. of the order of magnitude of 10 seconds, and the temperature were low (20–25°C).

Earlier (9) we investigated such a possible relationship, but we applied extraction times of 10 minutes (22°C) and 7 hours (44°C), because most extraction methods reported in the literature were in this range (7). No direct influence of the free-fat content on the dispersibility was observed, although below 20 % free fat, there was a tendency for the dispersibility to increase with decreasing amount of free fat. This is not surprising because the extraction times were too long, and the temperature was too high with the 7-hour extraction. Consequently in many cases the greater part of the extracted fat was not surface fat. For the same reason the data reported in the literature should not show such an effect and where they do, we ascribe the relationship to other factors such as the particle size and the homogenization which might have influenced both the dispersibility and the extractability of the fat.

There is no experimental evidence concerning the manner in which the dispersibility of spray-dried whole milk is influenced by the surface fat content.

c. The rising of cream, foaming and churning of the fat in milk reconstituted from powders. These quantities depend theoretically on the size distribution and the spatial distribution of the fat globules in the milk and their ability to coalesce to clusters or clumps. In the preceding paper (14) we showed that the size distribution of the fat globules in the reconstituted milk is not much different from that in the concentrated milk from which we prepared the powders. Some coalescence of fat globules took place during drying or during recon-

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stitution of milk from the powders.

On the other hand we observed earlier (9) that the above properties are not materially influenced by the free-fat content, although there was a positive correlation of the free-fat content both with the amount of churned butterfat on the surface of the reconstituted milk and the rising of the cream. The phenomena can be understood with our model: A relationship between f_e and the above properties need not exist, as in a number of cases the fat represented by the terms $f_l + f_d$ contributes but little to f_e. It is therefore not justified to consider a high free-fat content of spray-dried whole milk, as usually determined until the present time, as an indication of the occurrence of the above undesirable properties of the reconstituted milk.

d. The stickiness of milk powders. Of course the stickiness of spray-dried whole milk powders is only influenced by the surface fat f_s and not by the total amount of fat which can be extracted in some way or another from the powder particles. In Section 10.2 we showed that in many cases only a minor part of the total free fat f_e extracted in 10 minutes from spray-dried whole milk, is surface fat. It is therefore quite obvious that we found no relationship between f_e and the stickiness or rather the cohesion of our powders. Possibly such a relationship can be obtained with very short extraction times yielding a relatively large fraction of surface fat.

Summarizing the above we conclude that only the surface fat and the size distribution of the fat globules including clustering or clumping are of practical importance. Therefore it may be valuable to determine the amount of surface fat, at least approximately, with a very short extraction at room temperature, e.g. 10 seconds.

Clustering or clumping of fat globules can be judged best by a microscopical examination of the reconstituted milk. Qualitative information concerning the size distribution of the fat globules can be obtained in the same way, whereas more quantitative results can be obtained with a Coulter Counter.

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Summary

Many workers have observed that under standardized conditions only part of the fat present in spray-dried milk can be extracted by fat solvents. This fat is usually called 'free fat' and has been related to other powder properties which are of practical importance.

Contradictory results obtained by different workers have raised doubts concerning the practical significance of free fat. Moreover the explanation generally accepted in the literature, that free fat is 'unprotected fat' mainly situated on the particle surface, is not altogether satisfactory.

An experimental study of the properties of free fat and its relation to powder properties of practical significance was carried out. The results of this study were described in a series of papers in *Netherlands Milk and Dairy Journal* and are collected in this thesis.

In Chapter 1 a general outline of the problem and a brief review of the literature are given.

It seemed desirable to investigate the influence of the experimental conditions during the determination of the free-fat content because earlier authors used widely varying conditions. In Chapter 2 it is shown that the extraction time and temperature influence considerably the amount of fat which is extracted but its influence may depend strongly on the powder under investigation.

Because it was not clear which experimental conditions yielded free-fat contents relevant to other powder properties, two methods were usually applied, differing widely in contact time and extraction temperature.

Particle size is of major importance for the physical properties of most powders. In Chapter 3 two methods are described to determine the mean particle size and the particle size distribution of spray powders, viz gas permeametry and microscopic counting, respectively. With these methods the influence of certain process parameters on particle size and the influence of particle size on

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the free-fat content of spray-dried whole milk were studied. It is shown that the mean particle size increases inversely with $\sqrt{p}$, p being the spray pressure. Orifice diameters appeared to be of minor importance. Increasing the dry-solids content of the concentrated milk in the range of 30–45 % resulted in a reduction of the number of small particles. No influence of the particle size on the fat content and the moisture content was observed, but both the mean particle density and the free-fat content strongly increase with decreasing particle size.

It is suggested that the influence of some processing parameters on the free-fat content of spray-dried whole milk may be attributed to their influence on particle size.

With 20 powders, widely differing in free-fat content, the possible relationship between free fat and other powder properties of practical importance is investigated (Chapter 4). From the results the following conclusions were drawn: 1. There is no influence of the free fat on the development of oxidation flavour during 6 months' storage at 30°C in the presence of air; 2. The solubility of spray-dried whole milk is usually better if its free-fat content is higher, but probably there is no causal relationship between the two quantities; 3. Below a free-fat content of 20 % (of the fat) there is a tendency for the dispersibility to increase with decreasing amount of free fat. This is not the case above 20 % free fat. Because both particle size and homogenization may effect dispersibility as well as free-fat content, no causal influence of free fat on dispersibility could be observed; 4. Neither cream rising nor foam formation during reconstitution is materially influenced by the amount of free fat in the powder. Churning of the butterfat by vigorously stirring during reconstitution was observed only with powders containing much free fat, prepared from unhomogenized concentrated milk. No quantitative correlation was observed between the amount of churned butterfat and the free-fat content of the powder.

Chapter 5 treats the stickiness of spray-dried whole milk and a simple test to determine the cohesion of such powders is described. Good agreement between this cohesion and the visual observation of stickiness was found. It is shown that the cohesion of spray-dried whole milk increases with decreasing particle size as expected. Unexpected, however, was that the cohesion is independent of fat content in the range of 20–45 % fat, and of free-fat content. In spite of this, experiments at different temperatures showed that the milk fat is an important factor in the cohesion, and it is suggested that only a small amount of surface fat on the particles is already sufficient to give cohesion to whole milk powders. Probably fat contents higher than 20% result in more surface fat, but this does not increase the cohesion.

It is shown that an increase of moisture content decreases the cohesion in the range of 2–4%, but a strong rise of cohesion occurs in the range of 4–7%,

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probably due to increased plasticity of the powder particles and to lactose crystallization.

In Chapter 6 it is shown that the free-fat content decreases considerably when the moisture content of spray-dried whole milk is increased in the range of 2–8 %. The effect appeared to be reveısible. It is suggested that part of the fat is extracted from the milk powder particles via capillary pores or cracks, which close when the powder absorbs water.

With a scanning electron microscope photographs were taken of dried milk particles without water being used, this to avoid artefacts. The method is described in Chapter 7 and a few photographs are shown.

From measurement of the penetration speed of nitrogen into the powder particle porosity factor was calculated (Chapter 8). There appeared to be a strong correlation ($r = 0.94$) between the free-fat content and this particle porosity. From this observation it is concluded that the particle porosity is of major importance for the extraction of fat from milk powders.

Photographs taken with a scanning electron microscope show cracks and pores in particles with high porosity, whereas in less porous powder particles only surface folds and occasional cracks could be observed.

Possible explanations of particle porosity are discussed.

Chapter 9 contains the fat globule size distributions in concentrated milk and in milk reconstituted from whole milk spray powders with various free-fat contents as determined with a Coulter counter. It is concluded that the spraying of concentrated milk causes a considerable size reduction of the fat globules. Some coalescence of fat globules takes place during drying or during reconstitution of milk from the powders. A rather good relationship is obtained between the free-fat content of the powders and the percentage of fat present as fat globules > 2 μm in milk reconstituted from the same powders.

The phenomenon that only part of the fat in spray-dried whole milk can be extracted by fat solvents is usually explained by the assumption that this 'free fat' is unprotected surface fat.

In Chapter 10 it is shown that surface fat in such powders is dissolved in a few seconds by organic solvents. The amount of fat extracted by the majority of the extraction methods with much longer contact times applied until now, consists for only a minor part of surface fat in many cases. Experiments with spray powders consisting only of lactose and anhydrous butterfat show that fat globules without protein membranes can be protected by the amorphous lactose against fat solvents.

A new model for the occurrence of free fat in spray-dried whole milk, based on the accessibility of the fat in the powder particles, is proposed.

The relationship between fat content and free-fat content of spray-dried

whole milk is investigated, and the curves which were obtained are explained with the new model.

Finally the practical consequences of the model are discussed and compared with the results of earlier experiments. The conclusion is that only the surface fat is relevant because of its possible influence on dispersibility and the cohesion of spray-dried whole milk. This fat can be determined approximately with a very short extraction (e.g. 10 seconds) at room temperature.

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Samenvatting

Door vele onderzoekers werd waargenomen dat onder gestandaardiseerde omstandigheden slechts een deel van het vet aanwezig in vollemelkpoeders geëxtraheerd kan worden met organische oplosmiddelen.

Dit vet, dat doorgaans 'vrij vet' wordt genoemd werd reeds vroeg in verband gebracht met andere, voor de praktijk belangrijke, eigenschappen van melkpoeder, zoals de houdbaarheid, de dispergeerbaarheid, de oproming van melk uit melkpoeders en de plakkerigheid van deze poeders. In alle gevallen werd een hoog vrij-vetgehalte als nadelig beschouwd.

Tegenstrijdige resultaten, verkregen door verschillende auteurs, deden twijfel rijzen ten aanzien van de praktische betekenis van de aanwezigheid van vrij vet. Ook de vrij algemeen aanvaarde veronderstelling dat vrij vet bestaat uit onbeschermde vetbolletjes die samengevloeid zijn tot vet dat zich voornamelijk op het oppervlak van de poederdeeltjes bevindt, is, gezien sommige resultaten, onbevredigend.

Daarom werd een experimenteel onderzoek opgezet om de ware aard van het vrije vet in verstuivingsvollemelkpoeders te bestuderen en tevens om na te gaan of eerdergenoemde voor de praktijk belangrijke poedereigenschappen worden beïnvloed door het 'vrije vet'.

De resultaten van het onderzoek werden gepubliceerd in een tiental artikelen in het *Nederlands Melk- en Zuiveltijdschrift*. Deze artikelen zijn gebundeld tot een proefschrift en vormen daarin tien hoofdstukken.

In het eerste hoofdstuk wordt een algemene inleiding gegeven en tevens een beperkt literatuuroverzicht, dat betrekking heeft op de relatie tussen het vrij-vet gehalte en de fysische structuur van melkpoederdeeltjes. Tevens wordt de invloed van procesvariabelen op het vrij-vetgehalte van vollemelkpoeders behandeld.

Hoofdstuk 2 omvat een systematisch onderzoek naar de invloed van de bepalingsomstandigheden op de hoeveelheid vet die uit verstuivingsvollemelk-

poeders kan worden geëxtraheerd. Dit was gewenst omdat door andere auteurs onder sterk uiteenlopende omstandigheden werd geëxtraheerd, waardoor hun resultaten wellicht niet onderling vergelijkbaar zijn. Uit het onderzoek bleek dat een verlenging van de extractietijd en een verhoging van de extractie-temperatuur bij sommige poeders een grote invloed had op het gevonden vrij-vetgehalte, terwijl dat bij andere poeders niet het geval was.

Omdat niet bekend was onder welke omstandigheden een vrij-vetgehalte wordt bepaald dat van belang is voor andere poedereigenschappen, werd voor het onderhavige onderzoek vrijwel steeds gebruik gemaakt van twee methoden met zeer verschillende bepalingsomstandigheden, te weten een extractie bij kamertemperatuur gedurende 10 minuten en een Soxhlet-extractie (44°C) gedurende 7 uur, beide met petroleumether.

In Hoofdstuk 3 wordt de invloed van de deeltjesgrootte behandeld, nadat eerst de toegepaste meetmethoden werden beschreven en de resultaten daarvan besproken. De deeltjesgrootte bleek geen invloed te hebben op het vet- en vocht-gehalte van onder druk verstoven vollemelkpoeders. Daarentegen werd wel een belangrijke invloed geconstateerd van de deeltjesgrootte op het gehalte extraheerbaar vet. Aangezien tevens werd gevonden dat de verstuivingsom-standigheden in aanzienlijke mate de deeltjesgrootte van de poeders kunnen beïnvloeden, werd geconcludeerd dat de door andere onderzoekers gevonden invloed van de procesvariabelen op het vrij-vetgehalte van verstuivingsvolle-melkpoeders voor een belangrijk deel zal moeten worden toegeschreven aan de invloed van deze variabelen op de deeltjesgrootte.

Hoofdstuk 4 beschrijft het onderzoek naar een mogelijk verband tussen het vrij-vetgehalte en een aantal voor de praktijk belangrijke poedereigenschappen, waarvoor 20 poeders met sterk uiteenlopende vrij-vetgehalten werden gebruikt. Uit de resultaten werden de volgende conclusies getrokken:

1. Van een invloed van het vrij-vetgehalte op de ontwikkeling van de oxydatie-smaak tijdens 6 maanden bewaren bij 30°C (onder lucht) is niets gebleken;

2. De oplosbaarheid van verstuivingsvollemelkpoeders is doorgaans beter als het vrij-vetgehalte hoog is, maar het wordt betwijfeld of er een oorzakelijk verband tussen beide grootheden bestaat;

3. Als het vrij-vetgehalte lager dan 20% van (het vet) is, is er een tendens dat de dispergeergaarheid van het poeder beter is naarmate het vrij-vetgehalte daalt. Boven 20% is geen invloed geconstateerd. Door de melk voor het ver-stuiven te homogeniseren werd de dispergeerbaarheid sterk verhoogd, maar de oplosbaarheid sterk verlaagd. Ook in dit geval wordt betwijfeld of er een direct verband bestaat tussen vrij vet en dispergeerbaarheid, omdat zowel de deeltjesgrootte als de homogenisatie invloed hebben op beide groötheden.

4. Noch de oproming, noch de schuimvorming in melk uit vollemelkpoeder

vertonen een sterke correlatie met het vrij-vetgehalte.

5. Uitbotering trad op tijdens het met een sneldraaiende menger oplossen van melkpoeders, bereid uit niet gehomogeniseerde melk met veel vrij vet, maar niet als de ingedampte melk voor het verstuiven werd gehomogeniseerd. De hoeveelheid uitgekarnd botervet was klein vergeleken met de hoeveelheid vrij vet en tussen beide grootheden kon geen kwantitatieve correlatie worden waargenomen bij de gebruikte poeders.

In Hoofdstuk 5 wordt een eenvoudige methode beschreven om de bekende plakkerigheid van vollemelkpoeders te karakteriseren door een gemeten cohesie. Daarvoor werd gebruik gemaakt van de in de grondmechanica bekende zuiltjesproef. Tussen de resultaten van deze proef en de visueel geconstateerde plakkerigheid werd een goede overeenstemming gevonden.

Uit het onderzoek blijkt ook dat de cohesie van vollemelkpoeders in belangrijke mate afhangt van de vooraf daarop toegepaste druk en van de deeltjesgrootte, zoals overigens verwacht mocht worden. Tegen de verwachting in werd geconstateerd dat de cohesie niet afhangt van het vetgehalte in het gebied van 20–45 % vet of het vrij-vetgehalte van de poeders, indien de invloed van de deeltjesgrootte wordt geëlimineerd.

Ook onverwacht was dat de cohesie met toenemend vochtgehalte eerst sterk afneemt, maar bij 5 à 6 % vocht zeer sterk stijgt. Van dit laatste is de lactosekristallisatie vermoedelijk de oorzaak.

Uit experimenten bij verschillende temperaturen blijkt dat het vet in melkpoeders toch wel een belangrijke rol speelt bij de mate van plakkerigheid. Vermoedelijk veroorzaakt een geringe hoeveelheid oppervlaktevet reeds een aanzienlijke cohesie en bij een vetgehalte vanaf ca. 20 % is deze hoeveelheid reeds aanwezig, onafhankelijk van het vrij-vetgehalte.

De afname van de cohesie met toenemend vochtgehalte in het gebied van 2–5 % zou verklaard kunnen worden door aan te nemen dat oppervlaktevouwen en scheurtjes verdwijnen bij vochtopname.

In Hoofdstuk 6 wordt geconstateerd dat het vrij-vetgehalte van verstuivingsvollemelkpoeders belangrijk afneemt met toenemend vochtgehalte. Het effect bleek reversibel te zijn. Als verklaring wordt gegeven dat het vet voornamelijk uit de melkpoederdeeltjes wordt geëxtraheerd via capillairen en scheurtjes, die ontstaan tijdens het droogproces en weer dichttrekken bij vochtopname.

Het lag voor de hand te proberen met een electronenmicroscoop aan te tonen dat dergelijke capillairen en scheurtjes aanwezig zijn in de poederdeeltjes. Dit kon inderdaad worden aangetoond. De methode werd beschreven in Hoofdstuk 7, terwijl ook Hoofdstuk 8 een aantal foto's bevat die aanvullende informatie geven op andere metingen. Deze metingen betroffen de indringsnelheid van stikstof in deeltjes van verstuivingsvollemelkpoeders. Uit deze gemeten

indringsnelheid werd een poreusheidsfactor voor de poederdeeltjes berekend, die een sterke correlatie bleek te vertonen met het vrij-vetgehalte van de poeders. Het ontstaan van capillairen of scheurtjes wordt toegeschreven aan de omstandigheden tijdens het drogen van de poeders naar analogie van ervaringen in de keramische industrie.

Voor de extractie van het vet uit vollemelkpoederdeeltjes leek ook de vetbolletjesgrootte van belang te zijn. Daarom werd met behulp van een Coulter Counter de vetbolletjesgrootteverdeling gemeten in ingedampte melk en in melk verkregen door oplossen van vollemelkpoeder. Een en ander is beschreven in Hoofdstuk 9. Uit de resultaten bleek dat tijdens het verstuivingsdrogen van melk een aanzienlijke verkleining van de vetbolletjes optreedt en wel meer naarmate de verstuivingsdruk of de rotatiesnelheid van het wiel hoger is.

Er bleek een goede correlatie te bestaan tussen het percentage vet aanwezig in de vorm van vetbolletjes groter dan 2 μm en het gehalte extraheerbaar vet.

In Hoofdstuk 10 wordt aangetoond dat het vet op het oppervlak van melkpoederdeeltjes zeer snel oplost. Proeven met verstuivingspoeders, uitsluitend bestaande uit amorfe lactose en watervrij botervet, dus met vetbolletjes zonder eiwitmembranen, laten zien dat de vetvrije melkdrogestof aan de vetbolletjes een aanzienlijke bescherming kan bieden tegen vetoplosmiddelen.

De door vele onderzoekers gedane aanname dat 'vrij vet' in melkpoeders te danken is aan vetbolletjes met beschadigde membranen wordt verworpen, omdat daarvoor niet voldoende experimentele aanwijzingen bekend zijn. In de plaats daarvan wordt een natuurkundig model voor het extraheerbare vet in verstuivingsvollemelkpoeders voorgesteld. Dit model is gebaseerd op de bereikbaarheid voor oplosmiddelen van het vet in de poederdeeltjes. Vier gevallen worden onderscheiden.

1. oppervlaktevet; 2. vetbolletjes in de buitenlaag van de poederdeeltjes; 3. capillair vet, d.w.z. vetbolletjes die bereikt kunnen worden via capillairen of kleine scheurtjes in de poederdeeltjes; 4. oplosvet of 2e-echelon vet, bestaande uit vetbolletjes binnenin de deeltjes die bereikbaar worden als meer naar buiten gelegen vetbolletjes oplossen.

Met behulp van dit model wordt een verklaring gegeven van het gevonden verband tussen het vetgehalte en het vrij-vetgehalte van verstuivingsvollemelkpoeders. Ook de invloed van de homogenisatie van de melk en de deeltjesgrootte van de poeders wordt verklaard.

Tot slot worden de consequenties van het model voor de zuivelpraktijk besproken met als conclusie dat alleen de bepaling van het oppervlaktevet enige practische zin heeft in verband met de invloed van het oppervlaktevet op de plakkerigheid van vollemelkpoeders en de dispergeerbaarheid. Hiervoor zou een zeer korte extractietijd moeten worden gebruikt, bijv. 10 seconden.

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Curriculum vitae

De schrijver van dit proefschrift begon zijn studie in 1947 aan de Rijksuniversiteit te Groningen na in juni van dat jaar het diploma H.B.S.-B te hebben behaald in dezelfde stad. Aanvankelijk werd de studierichting Wis- en Natuurkunde, letter d, gekozen, maar in juni 1952 werd het candidaatsexamen, letter e, afgelegd. In september 1955 volgde het doctoraal examen Experimentele Natuurkunde met bijvak Scheikunde.

In de periode tussen september 1954 en augustus 1956 werd, in de functie van assistent bij de afdeling Theoretische Natuurkunde van het Natuurkundig Laboratorium te Groningen, experimenteel onderzoek verricht op het gebied van de optica onder leiding van prof. dr. F. Zernike.

Gedurende de militaire dienst van augustus 1956 tot augustus 1958 werd in De Bilt een opleiding gevolgd voor luchtvaartmeteoroloog. In aansluiting daarop werd in deze periode naast het weerdienstwerk enig wetenschappelijk onderzoek gedaan met als onderwerp 'het zicht'.

Van augustus 1958 tot september 1959 was de schrijver werkzaam als hoofd-assistent in het Natuurkundig Laboratorium van de R.U. te Groningen, belast met de leiding van het natuurkunde-practicum, en was hij lid van een kern-fysische werkgroep onder leiding van prof. dr. H. Brinkman.

Sinds 1 september 1959 is de auteur van dit proefschrift als natuurkundige verbonden aan het Research Laboratorium van de CCF te Leeuwarden. Daarnaast is hij vanaf 1 september 1960 leraar aan de Avondschool te Leeuwarden van het Nederlands Genootschap tot Opleiding van Leerkrachten voor het Beroepsonderwijs.